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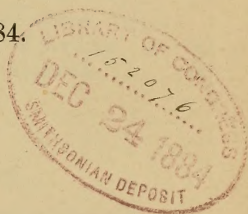
SIR WILLIAM THOMSON, KNT. LL.D. F.R.S. &c.

AND

WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

" Meditationis est perscrutari occulta ; contemplationis est admirari perspicua . . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

—" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.
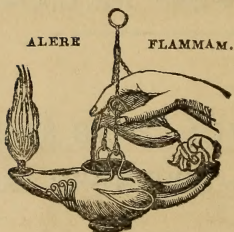
CONTENTS OF VOL. XVIII.

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PLATES.

I. *The Periodic Law, as illustrated by certain Physical Properties of Inorganic Compounds.* By Thomas Carnelley, *D.Sc., Professor of Chemistry in University College, Dundee*[*].

[Plate I.]

THE object of the present paper is :—(1) To illustrate the truth of the Periodic Law by means of the melting- and boiling-points and heats of formation of the halogen compounds of the elements. (2) To apply the facts thus obtained to the calculation of unknown melting- and boiling-points. (3) To show how a knowledge of the melting- and boiling-points of the compounds of an element may be used for the determination of its atomic weight, when the application of the methods of specific heat and vapour-density do not give satisfactory results. (4) To show how the position of an element in the general classification may be inferred from the known melting- and boiling-points of its compounds.

It is only within the last few years that the number of melting- and boiling-points determined for inorganic compounds has rendered it possible to draw any conclusions as to the laws which govern them. This has been chiefly due to the difficulty of determining the melting- and boiling-points of bodies which fuse or boil only at temperatures which are beyond the range of an ordinary thermometer. This difficulty

* Communicated by the Author.

has now, however, been in great part removed; for in several previous papers (Journ. Chem. Soc. xxix. p. 493, xxxiii. pp. 273 and 283 *, xxxv. p. 564 *, xxxvii. p. 125 *) methods have been proposed for determining both high melting- and high boiling-points.

I. Illustration of the Periodic Law.

The Periodic Law states :—(1) That the properties of the *elements* are a periodic function of their atomic weights; (2) that the properties of the *compounds* of the elements are a periodic function of the atomic weights of their constituent elements.

It is this second part of the law which we shall endeavour to illustrate. For this purpose we shall make use of the melting- and boiling-points and heats of formation of the chlorides, bromides, and iodides of the elements. The term *normal* chloride, bromide, or iodide will be used to indicate halogen compounds of the form, represented thus :—LiCl, $BeCl_2$, BCl_3, CCl_4, NCl_3, OCl_2, FCl, for members of Mendeljeff's second series. In all the tables the symbols given to still undiscovered elements are those proposed by Mendeljeff in his memoir on the Periodic Law (*Ann. Chem. Pharm.* Suppl. 1870–72, p. 151). In addition to the experimental values given in Table I. A, melting- and boiling-points (see Table IX.), calculated by a method to be presently explained, are also inserted in the tables, in order that the latter may be as complete as possible. In all cases the heat of formation given is the heat evolved by the combination of one atom of Cl or its equivalent.

Now, however we may arrange the melting-points, boiling-points, or heats of formation of the normal halogen compounds of the elements, provided only that we arrange them systematically, we always find that certain definite and regular relations may be traced between them. Some of the more important of these relations are as follows † :—

Relation 1. *If the elements be arranged in the order of their atomic weights, then the melting-points, boiling-points, and heats of formation of their halogen compounds rise and fall periodically.* These periods correspond exactly with the series of elements in Table I.‡, the maxima occurring at the positive and the minima at the negative end of each series. The exceptions

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* In conjunction with Prof. Carleton-Williams.

† Throughout this paper all temperatures are reckoned from the absolute zero ($-273°$ C.).

‡ Table I. represents the natural classification of the elements according to Mendeljeff's arrangement, and is given here for reference.

Table I.—Natural Classification of the Elements. (After Mendeljeff.)

Groups …	I.	II.	III.	IV.	V.	VI.	VII.	Group VIII.
Series.	Monads.	Dyads.	Triads.	Tetrads.	Triads or Pentads.	Dyads or Hexads.	Monads or Heptads.	
1. …	H=1							
2. …	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	
3. …	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5	{ Fe=56, Co=59, Ni=59, (Cu=63).
4. …	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	
5. …	Cu=63	Zn=65	Ga=69	EkaSi=72(?)	As=75	Se=79	Br=80	{ Ru=104, Rh=104, Pd= 106, (Ag=108).
6. …	Rb=85	Sr=87	Yt=89	Zr=90	Nb=94	Mo=96	……	
7. …	Ag=108	Cd=112	In=113	Sn=118	Sb=120	Te=125	I=127	
8. …	Cs=133	Ba=137	La=139	Ce=142	Di=147	Tb=149 (?)	……	——, ——, (——).
9. …					Er=166 (?)	……	……	
10. …	……	……	Yb=173	…………	Ta=182	W=184	……	{ Os=193, Ir=193, Pt= 195, (Au=197).
11. …	Au=197	Hg=200	Tl=204	Pb=207	Bi=210	……	……	
12. …	……	……	……	Th=234	……	U=240	……	——, ——, (——).

TABLE I. A.

	Melting-point.	Boiling-point.	Authority.
Cl	198	240	Berthelot ; Regnault.
ClBr	......	286	*Ann. Chem. Pharm.* clxxxix. p. 208.
ClI.................	298	373	Thorpe.
Br	251	331	Andrews.
BrI	309	390	{ *Ann. Chem. Pharm.* clxxxix. p. 203 ; and Macivor.
I	383	473	Exner, Stas.
OCl_2	......	253	Pelouze.
SCl_2	......	337	Dumas.
NCl_3	......	344	Pelouze and Frémy.
PCl_3	......	351	Dumas.
PBr_3	......	444	Baudimont and Pierre.
PI_3	328	......	Corenwinder.
$AsCl_3$..............	......	405	Dumas.
$AsBr_3$	295	493	Serullas.
AsI_3	419	677	Carnelley and Williams.
$SbCl_3$..............	345	496	Kopp.
$SbBr_3$	363	549	,,
SbI_3	438	693	Macivor ; Carnelley and Williams.
$BiCl_3$..............	503	703	Muir ; Carnelley and Williams.
$BiBr_3$	480	749	Carnelley and Williams.
CCl_4	......	351	Regnault.
CBr_4	364	462	Bolas and Groves.
$SiCl_4$	......	331	Haagen.
$SiBr_4$	260	426	Serullas ; Pierre.
SiI_4	393	563	Friedel.
$TiCl_4$	......	408	Duppa.
$TiBr_4$..............	312	503	,,
TiI_4	423	633	Hautefeuille.
$SnCl_4$..............	......	388	Pierre.
$SnBr_4$	303	474	Carnelley and O'Shea.
SnI_4	419	568	Personne.
$AlCl_3$..............	......	453	Liebig.
$AlBr_3$	363	533	Deville and Troost.
AlI_3	398	623	,, ,,
BCl_3	......	290	Wöhler and Deville.
BBr_3	......	363	,, ,,
$GaCl_3$	346	......	Boisbaudran.
LiCl	870	......	Carnelley.
LiBr	820	......	,,
LiI.................	719	......	,,
KCl	1007	......	,,
KBr	972	......	,,
KI..................	907	......	,,
RbCl	983	......	,,
RbBr..............	956	......	,,
RbI	915	......	,,
$CaCl_2$	992	......	,,
$CaBr_2$	949	......	,,
CaI_2	904	......	,,
$SrCl_2$..............	1098	......	,,
$SrBr_2$..............	903	......	,,
SrI_2	780	......	,,
$BaCl_2$..............	a. 1181	......	,,

Table I A. (*continued*).

	Melting-point.	Boiling-point.	Authority.
$BaBr_2$	1085	......	Carnelley.
NaCl	1045	......	,,
NaBr	981	......	,,
NaI	901	......	,,
Cu_2Cl_2	707	......	,,
Cu_2I_2	874	......	,,
AgCl	724	......	,,
AgBr	700	......	,,
AgI	800	......	,,
$MgCl_2$	981	......	,,
$MgBr_2$	971	......	,,
$ZnCl_2$	535	953	Braun; Carnelley and Williams.
$ZnBr_2$	667	972	Carnelley; ,, ,,
ZnI_2	719	......	,,
$CdCl_2$	814	......	,,
$CdBr_2$	844	......	,,
CdI_2	677	......	,,
$HgCl_2$	561	576	Carnelley and Williams.
$HgBr_2$	517	592	,, ,,
HgI_2	514	622	,, ,,
CsCl	904	......	,, ,,

to this rule occur either at the maxima or at the minima (*i. e.* at the turning-points) of Meyer's curve of the elements (*Mod. Theor. der Chem.*), or, in other words, with the tetrad elements C, Si, Ti, &c., or the positive monad elements Rb, Ag, and Cs. And further, the *odd* tetrad elements, when they are exceptions, always have a lower melting-point or boiling-point, whilst the *even* tetrad elements have a higher melting- or boiling-point than would be required by the rule. These instances, therefore, must be looked upon, not as exceptional, but rather as confirming the truth of the Periodic Law; for they themselves occur regularly and periodically.

The above facts are illustrated by Table II., which exhibits the values for the chlorides, bromides, and iodides of the elements from Li to Ti. In the first column the elements are arranged according to the size of their atomic weights; in the second, third, and fourth columns are given the melting-points, boiling-points, and heats of formation of the chlorides, and in the following columns those of the corresponding bromides and iodides.

This relation is rendered still more evident by the curve shown in the diagram (Plate I.), in which the melting-points of the halogen compounds are represented by the ordinates, and the atomic weights of the positive elements by the abscissæ.

RELATION 2. *In passing from the first and second members*

TABLE II.—Illustrating Relations 1, 2, 3.

	CHLORIDES.			BROMIDES.			IODIDES.		
	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.
Li	870	......	94000	820	......	......	719		
Be	874	......	......	874	......	......	771		
B	210	290	36166	271	363	24366	397	493	
C	231	351	......	364 ?	462	......	420	620	
N	200	344	......	244	439	......	322	585	
O	199	251	......	237	346	......	310	465	
F	189	215	......	218	270	......	264	359	
Na	1045	......	97700	981	......	90600	901	......	74100
Mg.........	981	......	75500	971	......	70000	896	......	54000
Al	340	453	52000	366	533	42830	398	623	27870
Si	205	331	39400	260	426	30100	393	563	14000
P	200	351	25266	252	444	18200	328	575	8900
S............	199	337	......	240	406	......	315	528	
Cl	198	240	......	229	286	......	298	373	
K	1007	......	104600	972	......	99000	907	......	85200
Ca	992	......	84800	949	......	75600	904	......	59100
Sc	236	334	......	293	407	......	404	528	
Ti	246	408	......	312	503	......	423	633	

of each series (the difference between which is comparatively small) to the third member, there is a sudden drop in both melting-point and boiling-point; whilst, on passing from the third on to the seventh, the decrease is far more gradual. (See Table II. and Plate I.)

RELATION 3. (a) *For the third, fourth, fifth, sixth, and seventh groups of elements, the melting-point and boiling-point increase as we pass from the chloride to the bromide and thence to the iodide.*

(b) *For the* even *members of the first and second groups, the opposite relation holds good.*

(c) *In all cases the heat of formation diminishes from chlorides to iodides.*

For illustration of the above, see Table II. and Plate I.; also Table III., in which are arranged the elements belonging to the fourth, or carbon-group. The even members of the group are printed in ordinary and the odd members in black figures. According to Mendeljeff, it is only the odd members which can be strictly compared with the odd, or the even members with the even, and not the odd members with the even; and this, as will be seen, is fully borne out by a comparison of their melting- and boiling-points.

Table III.—Illustrating Relations 3 and 4.

	Chlorides.			Bromides.			Iodides.		
	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.
C	231	351	......	364(?)	462	......	420	620	
Si	205	331	39400	260	426	30100	393	563	14000
Ti	246	408	......	312	503	......	423	633	
EkaSi ...	218	339	......	271	428	......	399	565	
Zr	326	495	......	367	555	......	455	681	
Sn	254	389	31700	303	474	28850	419	568	20000
Ce	409	556	......	434	611	......	515	735	
EkaSn ..									
EkaCe ...									
Pb	338	498	......	372	555	......	498	659	

Relation 4. (a) *For the chlorides, bromides, and iodides of Groups* III. *to* VII., *and of the even members of the second group, the melting-point and boiling-point increase with the atomic weight of the positive element.*

(b) *For the odd members of the first and second groups, the melting-point and heat of formation diminish as the atomic weight of the positive element increases.*

(c) *For the even members of the first group, the melting-point and heat of formation increase from* Li *to* K, *and then diminish to* Cs.

For illustration see Table III.

Relation 5. *The differences between the boiling-points of the chlorides and bromides, bromides and iodides, chlorides and iodides are greater than those between the corresponding melting-points.*

Thus :—

	Boiling-point.	Melting-point.
$SnCl_4$	389°	254°
$SnBr_4$	474	303
Difference	= 85 is greater than	49
SiI_4	563	393
$SiBr_4$	426	260
Difference	= 137 is greater than	133

See also Tables IV. and V.

Relation 6. *The differences referred to in Relation 5, for both melting- and boiling-points, increase algebraically from the*

first member of each series to the fourth or middle (tetrad) member, and then diminish to the seventh or last member.

For illustrations see Table IV.

TABLE IV.—Illustrating Relations 5, 6, and 7.

	Br.—Cl.			I.—Br.			I.—Cl.		
	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.
Na	−64	......	7100	−80	......	16500	−144	......	23600
Mg.........	−10	......	5500	−75	......	16000	− 85	......	21500
Al	26	80	9170	32	90	14960	58	170	24130
Si	55	95	9300	133	137	16100	188	232	25400
P	52	93	7066	76	131	9300	128	224	16368
S	41	69	......	75	122	......	116	191	
Cl	31	46	......	69	87	......	100	133	

TABLE V.—Illustrating Relations 5, 7, and 8.

	Br.—Cl.			I.—Br.			I.—Cl.		
	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.	Melting-point.	Boiling-point.	Heat of formation.
C	133?	111	......	56?	158	......	189	269	
Si	**55**	**95**	**9300**	**133**	**137**	**16100**	**188**	**232**	**25400**
Ti	66	95	......	111	130	......	177	225	
EkaSi ...	**53**	**89**	......	**128**	**137**	......	**181**	**226**	
Zr	41	60	......	88	126	......	129	186	
Sn	**49**	**86**	**2850**	**116**	**94**	**8850**	**165**	**180**	**11700**
Ce	25	55	......	81	124	......	106	179	

RELATION 7. *The difference between the melting-, or boiling-points, or heats of formation of the bromide and chloride of an element is less than that between those of its iodide and bromide, and the latter less than that between those of its iodide and chloride.* For illustrations see Tables IV. and V.

RELATION 8. *The differences between the melting-points, or boiling-points, or heats of formation diminish as the atomic weight of the positive element increases, except in the case of the melting-points of the even members of the second group, for which the opposite relation holds good.*

This is illustrated by Table V., which represents the carbon-silicon group of elements, the even members of the group being given in ordinary and the odd members in black figures.

RELATION 9. (a) *For members of the third, fourth, fifth, sixth, and seventh groups, and for* even *members of the second group, the differences between the melting-points, and also between the boiling-points of the chlorides, or bromides, or iodides of the odd and also of the even members of each group diminish as we pass from the chlorides to the bromides and thence to the iodides, and* (b) *increase as the difference between the atomic weights of the two positive elements increases. With* even *members of the first group, exactly the reverse is the case.*

To exhibit this relation we may use the arsenic group, as represented in the following Table :—

TABLE VI.—Illustrating Relation 9.

I.	Difference of atomic weights of elements in I.	CHLORIDES.		BROMIDES.		IODIDES.	
		Melting-point.	Boiling-point.	Melting-point.	Boiling-point.	Melting-point.	Boiling-point.
As–P	44	44	54	43	49	91?	102?
Sb–As	47	101	91	68	56	19	-16
Sb–P	91 or 89 *	145	145	111	105	110	118
Bi–Sb..........	88 or 90 *	158	207	117	200	116	171
Bi–As.........	135	259	298	185	256	135	187
Bi–P	179	303	352	228	305	226	289

* If Sb = 120.

RELATION 10. (a) *The differences between the melting-points or boiling-points of the chlorides, or bromides, or iodides of the elements of Groups* III. *to* VII., *and those of the seventh or halogen group increase algebraically from the chlorides to the bromides and thence to the iodides.*

(b) *With* even *members of the first and second groups these differences diminish from chlorides to iodides.* (See Table VII.)

RELATION 11. *The differences referred to under Relation* 10 *for Groups* III. *to* VII. *increase as the algebraic difference between the atomic weights of the positive elements increases.* (See Table VII.)

For members of the first and second groups no rule can be laid down.

RELATION 12. *The above differences (Relation* 10) *between the boiling-points are algebraically greater than those between the corresponding melting-points.* (See Table VII.)

The above twelve Relations (together with a few others of less importance) can at present be applied in no less than 3248 cases. Of these, 180 (or about 5 per cent.) are excep-

TABLE VII.—Illustrating Relations 10, 11, and 12.

I.	Difference of atomic weights of elements in I.	CHLORIDES.		BROMIDES.		IODIDES.	
		Melting-point.	Boiling-point.	Melting-point.	Boiling-point.	Melting-point.	Boiling-point.
P–I............	−96	−98	−22	−57	54	−55	102
As–I	−52	−54	+32	−14	103	+36	204
P–Br	−49	−29	65	+ 1	113	19	185
P–Cl	− 4·4	+ 2	111	23	158	30	202
Sb–I	− 4·5	47	123	54	159	55	220
As–Br	− 4·8	15	119	44	162	110	287
As–Cl.........	+39·5	46	165	66	207	121	304
Sb–Br	42·0	116	210	112	218	129	303
Sb–Cl	86·5	147	256	134	263	140	320
Bi–I	83·0	205	330	171	359	171	391
Bi–Br.........	130·0	274	417	229	418	245	474
Bi–Cl	174·5	305	463	251	463	256	491

(* marks are placed at the rows P–Cl/Sb–I/As–Br and Sb–Cl/Bi–I)

tions and do not obey the rules. This is a very small number of exceptions, and especially so if we bear in mind the following considerations :—

(1) The numbers obtained by different observers for the melting-point or boiling-point of one and the same substance vary somewhat in many cases, and considerably in some few. Consequently it is probable that many of the above exceptions are due to errors in the experimental melting-points and boiling-points.

(2) Several of the experimental values are somewhat uncertain, as is the case with the boiling-point of SCl_2 as found by Dumas and the boiling-point of NCl_3 as found by Pelouze and Frémy ; whilst it is probable that some of the compounds, the boiling-points of which have been determined, boil under ordinary circumstances with slight decomposition, which would of course produce a corresponding error in the boiling-point. This is the case with CBr_4 and some others.

(3) The boiling-points of several of the compounds have only been determined within certain limits, and yet the means of these limits have been employed in the construction of the tables, and these would of course produce corresponding, though small, errors.

(4) Most of the above exceptions, however, may be ascribed

* The differences in the second column at these points do not follow exactly the order of size. It is easily seen, however, that they are so very close together that slight errors in the atomic weights used (viz. P=31, Sb=122, As=75, Bi=210, Cl=35·5, Br=80, I=127) might easily affect the arrangement, as the following atomic-weight determinations show :— Bi=208 (Schneider), 210 (Dumas) ; Sb=120 (Schneider), 122·5 (Dexter), 122 (Dumas), 122·3 (Kessler), 120 (Unger), 120 (Cooke).

to the fact that, though the method to be presently described of calculating melting-points and boiling-points does not give definite points, but only limits between which the true melting-point or boiling-point will lie, yet in the construction of the tables the mean only of these has been used in order to avoid complication.

(5) No less than 73 out of the above 180 exceptions are due to the melting-point or boiling-point of the following eight substances being too high or too low :—CBr_4 and $AlCl_3$, the melting-points of which are too high ; AlI_3*, $SrBr_2$, SrI_2, and PI_3, the melting-points of which are too low ; AsI_3, the boiling-point of which is too high ; and SnI_4, AlI_3*, and PI_3, the boiling-points of which are too low. It is intended to re-determine at the earliest opportunity the melting-points and boiling-points of these compounds, and especially to observe whether they melt or boil with decomposition or not.

General Conclusions to be drawn from the above twelve Relations as to the Laws which govern the Melting- and Boiling-Points and Heats of Formation of the Normal Halogen Compounds of the Elements.

I. *If in a series of binary normal compounds one of the elements be common to all, then the melting-points, boiling-points, and heats of formation are periodic functions of the atomic weight of the other element.*

See Table II. and Plate I.

II. *The influence of the halogen on these same three physical properties increases with the number of its atoms in the compound.*
Thus :—

		Melting-point.				Melting-point.
PBr_3	=	252°		$SiBr_4$	=	260°
PCl_3	=	200		$SiCl_4$	=	205
		52				55

Here the difference between the melting-points of the compounds containing four atoms of halogen is greater than between those of the compounds containing only three. (Compare also Relation 6.)

III. *In any normal halogen compound the influence of either*

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* The numbers used for AlI_3 in the construction of the tables of relations were those obtained by Deville and Troost, viz. melting-point $=125°$, boiling-point$=350°$. Since writing the above I have found that Weber obtained the following :—melting-point = above 185°, boiling-point = above 359°, thus confirming the supposition that Deville and Troost's numbers are too low.

of the elements on the melting- or boiling-point increases with its own atomic weight and decreases with the atomic weight of the other element. Thus :—

Melting-point.			Melting-point.	
PBr_3	=	$252°$	PBr_3	=	$252°$
$AsBr_3$	=	295	PI_3	=	328

In each of the above pairs of compounds, which contain one element in common, it is seen that the melting-point increases with the atomic weight of the variable element, and that whether the latter be the positive or negative constituent, thus showing that the influence of an element on the melting-point of one of its compounds increases with its own atomic weight. The fact that the influence of an element on the melting-point or boiling-point of its compounds increases with its own atomic weight has been known for a long time with regard to some *few* series of compounds ; but I am not aware that it has been pointed out as of general application to *all* the elements of Groups III. to VII. For the *even* members of Groups I. and II. and for Na and Mg the influence is always of the opposite kind.

That the influence decreases with the atomic weight of the other element is shown by the following examples :—

Melting-point.			Melting-point.	
PBr_3	=	$252°$	$SbBr_3$	=	$363°$
PCl_3	=	200	$SbCl_3$	=	345
		52			18

Here the substitution of Br for Cl produces a larger increase in the melting-point in the case of the P than in that of the Sb compound, the atomic weight of P being less than that of Sb.

Again :—

Melting-point.			Melting-point.	
$SnBr_4$	=	$303°$	SnI_4	=	$419°$
$SiBr_4$	=	260	SiI_4	=	393
		43			26

As before, the substitution of Sn for Si produces a greater influence on the melting-point in the case of the bromides, *i. e.* where the atomic weight of the negative element is the least. (Compare also Relations 3, 4, 7, 8, and 9.)

Conclusion III. applies only to Groups III. to VII.

IV. (*a*) Where the melting- or boiling-point or heat of formation *increases* from chlorides to iodides, these physical

properties of the bromide are always *less* than the mean of those of the chloride and iodide, thus :—

		SbCl$_3$.	SbBr$_3$.	SbI$_3$.
Melting-point	=	345°	363°	438°

Mean of the melting-points of the chloride and iodide = 391°.

Whereas, when they *decrease* from chlorides to iodides, the physical properties of the bromide are always *greater* than the mean of those of the chloride and iodide, thus :—

		NaCl.	NaBr.	NaI.
Melting-point	=	1045°	981°	901°

Mean of the melting-points of the chloride and iodide = 973°.

(*b*) The melting- or boiling-points of the halogen compounds of the middle member of three consecutive elements of the same group (proved only for Groups III. to VII.) are always *less* than the mean of those of the other two, thus :—

		PBr$_3$.	AsBr$_3$.	SbBr$_3$.
Boiling-point	=	351°	444°	575°

Mean of the boiling-points of PBr$_3$ and SbBr$_3$ = 463°.

From the above it follows that :—

(1) *The melting-point, boiling-point,* **and heat of formation of** *a bromide are always nearer to those of the chloride than to those of the iodide.* (2) *The melting- and boiling-points of the halogen compounds of the middle member of three consecutive elements of the same group are always nearer to those of the compounds of the first member* (i. e. *the one with the lowest atomic weight*) *than to those of the last member.* This probably depends on the fact that the atomic weight of Br is less than the mean of those of Cl and I ; and that the atomic weight of the middle member of three consecutive elements of the same group is always less than the mean of those of the other two elements; thus :—

Cl = 35·5	P = 31	C = 12	K = 39
I = 127·0	Sb = 122	Zr = 90	Cs = 133
Mean = 81·25	Mean = 76·5	Mean = 51	Mean = 86
Br = 80	As = 75	Ti = 48	Rb = 85·5

V. The melting-points of the halogen compounds of the first and second groups are widely separated from those of the other groups (see Relation 2 and Plate I.), there being, in fact, a great jump from members of the third to those

of the first and second groups. In some cases, too, there appear to exist relations between the melting-points of the *even* members of these two groups different from those which exist between the other groups. The compounds of the elements usually placed in the *odd* division of the first and second groups are generally altogether irregular. In the case of the *odd* members of the first group this may be explained to some extent by the fact that it is very uncertain whether Ag, Cu, and Au really belong to the same group as Na. This was pointed out by Mendeljeff in his original memoir, in which he places these metals provisionally in both the first group along with Na, and in the eighth group along with Fe, Pd, Pt, &c.

II. Calculation of Melting- and Boiling-Points by the Method of Limits.

It will be readily seen that the relations referred to in the foregoing pages may be made the basis of a method for calculating (within certain limits) melting- and boiling-points which have not been *experimentally* determined. Thus, take the case of the boiling-point of $AsBr_3$. Supposing we know the boiling-points of $AsCl_3$ and AsI_3, then, according to Relation 3, the boiling-point of $AsBr_3$ lies between those of $AsCl_3$ and AsI_3; again, the boiling-point of $AsBr_3$, according to Relation 4, lies between those of PBr_3 and $SbBr_3$. We thus obtain a number of limits between which the boiling-point of $AsBr_3$ must lie; and by selecting from all of them the lowest superior and the highest inferior limit, we obtain two limits between which the boiling-point of $AsBr_3$ lies, and these limits are generally very near together; so that by proceeding in this way we may calculate the melting- or boiling-point of a substance within a very few degrees. Thus, if $x=$ the boiling-point of $AsBr_3$, then

By Relation 1, $x < 972$, but > 331.
  ,,   ,,   3, $x < 677$, but > 405.
  ,,   ,,   4, $x < 549$, but > 444.
  ,,   ,,   5, $(x-405) < 124$, but > 51.
  ,,   ,,   6, $(677-x) > 59$.
                 $(x-405) > 45$.
  ,,   ,,   7, $(x-405) < (677-x)$.
                 $(677-x) < 272$.
  ,,   ,,   8, $(x-405) < 93$, but > 53.
  ,,   ,,   9, $(x-444) < 54$.
                 $(549-x) < 91$, but > 49.
                 $(749-x) < 298$, but > 200.

By Relation 10, $(x-390) > 32$, but < 204.
                $(x-331) > 119$, but < 287.
                $(x-286) > 165$.

,,   ,,   11, $(x-390) > 54$, but < 113.
                $(x-331) > 159$, but < 207.
                $(x-286) > 162$, but < 218.

,,   ,,   12, $(x-390) > -14$.
                $(x-331) > 44$.
                $(x-286) > 22$.

We thus obtain no less than eighteen inferior and fifteen superior limits for the boiling-point of $AsBr_3$, none of which overlap ; and as of these the highest inferior limit $= 490$ and the lowest superior limit $= 498$, therefore the boiling-point of $AsBr_3 = (490-498)°$, mean $= 494°$. The boiling-point, as found by experiment, $= 493°$.

In order to test this method of calculation completely *all* the *known* melting-points and boiling-points of the normal

Table VIII.

Calculation of known Melting-Points and Boiling-Points.

Substance.	Calculated melting-point.		Melting-point by experiment.	Calculated boiling-point.		Boiling-point by experiment.
	Limits.	Mean.		Limits.	Mean.	
ClBr	......	......	......	285–286	286	286
BrBr	250–257	253	251	327–332	330	331
IBr	308–310	309	309	389–391	390	390
PBr_3	......	......	......	439–445	442	444
$AsBr_3$ ...	309–310	309	295	490–498	494	493
$SbBr_3$......	356–364	360	363	548–552	550	549
$BiBr_3$......	514–514	514	480	749–756	752	749
CBr_4	271–312	292	364	458–503	480	462
$SiBr_4$	257–277	266	260	424–429	426	426
$TiBr_4$......	295–343	319	312	493–507	500	503
$SnBr_4$ ...	325–344	334	303	434–452	443	474
Al_2Br_6 ...	312–324	318	363	503–536	520	533
BBr_3	......	......	......	351–401	376	363
$CaBr_2$ ...	957–969	963	949	......	......	......
$SrBr_2$ ...	939–956	947	903	......	......	......
$BaBr_2$ ...	above 857	a. 857	1085	......	......	......
$MgBr_2$ ...	917–981	949	971	......	......	......
$ZnBr_2$ ...	554–627	591	667	897–953	925	972
$CdBr$ ...	above 800	a. 800	844	......	......	......
$HgBr_2$ ...	537–561	549	517	576–599	588	592
LiBr	795–835	815	820			
KBr	964–964	964	972			
RbBr......	949–972	960	956			
NaBr......	973–981	977	981			
AgBr......	684–754	719	700			

halogen compounds of the elements have been calculated. The results obtained in the case of the bromides are given in Table VIII. p. 15. In the few cases where overlapping limits occur those limits are taken as correct, in favour of which there are the greater number of limits, the others being rejected.

In this way it has been found that the average differences of the calculated limits from the experimental values were :—

Per cent.

For the boiling-points of Groups III.–VII. = $\pm$ 4°·8 C., or 1·0

,,   ,,   ,,   I. & II. = $\pm$ 4°·0   or 0·6

For the melting-points of Groups III.–VII. = $\pm$ 15°·0   or 4·2

,,   ,,   ,,   I. & II. = $\pm$ 15°·0   or 1·8

The size of the average error is due chiefly to exceptionally great differences in but a few cases.

For some compounds the number of inferior or superior limits, or both, is very small; and therefore the error in these instances is chiefly due to this source. It is to be remarked that an error in any *one* of the data used in the construction of the tables employed in the calculations may produce a corresponding or even greater error in the calculated melting-points or boiling-points of *several* other bodies. Most of the errors in the above calculated values may be ascribed therefore to errors in the experimental numbers of but a very few substances. It must not be forgotten that all the calculation really gives is the limits between which a substance melts or boils, and not the exact melting- or boiling-point.

Calculation of Melting- and Boiling-points not yet experimentally determined.—By the method just described, a large number of unknown melting- and boiling-points have been calculated, and it is left to the future to decide whether these predictions are correct or otherwise.

In many cases the values have been calculated in two ways :—(1) By using experimental data only ; (2) by using *both* experimental and calculated data ; whilst for others the experimental data are so few in number, that it has only been possible to make the calculation by using both experimental and calculated data. The results obtained are given in the following table.

TABLE IX.

Throughout this table the positions assigned to the elements for the purpose of calculation are those given in Table I.

Substance.	Experimental data only used.		Experimental and calculated data used.	
	Melting-point.	Boiling-point.	Melting-point.	Boiling-point.
$CsCl$	b. 959	....	b. 959	
$CsBr$	b. 940	....	b. 940	
CsI	b. 923	....	b. 923	
$CuBr$	774–790	....	774–790	
MgI_2	891–901	....	891–901	
$BaCl_2$	....	....	$(1280–1351)^1$	
BaI_2	656–962	....	904–962	
$BeCl_2$	820–870	....	820–870	
$BeBr_2$	719–820	....	802–820	
BeI_2	423–719	....	766–777	
BCl_3	b. 290	....	205–215	
BBr_3	260–363	....	260–282	
BI_3	393–719	a. 563	393–401	465–521
CCl_4	$(253–276)^2$	....	215–246	....
CI_4	$(389–398)^3$	616–623	$(418–423)^4$	616–623
NCl_3	b. 245	....	199–200	....
NBr_3	237–258	434–444	240–248	434–444
NI_3	317–328	577–593	317–328	577–593
OCl_2	198–248	....	198–200	....
OBr_2	b. 258	344–363	232–243	344–348
OI_2	298–328	373–563	298–322	439–492
FCl	b. 243	b. 253	180–199	189–240
FBr	b. 364	253–363	199–237	253–286
FI	....	a. 253	237–291	346–373
$AlCl_3$	334–346	....	334–346	....
$SiCl_4$	$(198–230)^5$	....	198–211	....
PCl_3	198–228	....	198–201	....
PBr_3	251–254	....	$(251–254)^6$	....
PI_3	....	537–677	....	$(563–588)^7$
SCl_2	198–243	....	198–200	....
SBr_2	229–258	351–373	229–252	383–430
SI_2	$(298–328)^8$	470–563	314–316	493–563
$ClBr$	224–235	....	....	....
$ScCl_3$	....	....	232–241	331–336
$ScBr_3$	....	....	293–293	407–408 [9]
ScI_3	....	....	399–408	518–537

[1] Melts above 1150°; but how much above is not known.

[2] Possibly below 248°, as the limit 253° depends on the melting-point of CBr_4, which is exceptionally high.

[3] Very uncertain, perhaps better take above 389°.

[4] Omitting all the limits depending on the melting-point of CBr_4.

[5] Does not solidify at 253°.

[6] These limits may be too high; some of the data seem to indicate that it is near 205°.

[7] Somewhat uncertain.   [8] Does not solidify at 333°.

[9] If Mendeljeff's prediction (*loc. cit.*) be correct, that Scandium chloride (Ekaboron chloride) will boil above $AlCl_3$ and be solid at the ordinary temperature, then these values will be too low. They are all based on the values for the halogen compounds of Boron.

Table IX. (*continued.*)

Substance.	Experimental data only used		Experimental and calculated data used.	
	Melting-point.	Boiling-point.	Melting-point.	Boiling-point.
$TiCl_4$	217–248	....	244–248	....
$GaCl_3$	....	496–499	....	496–499
$GaBr_3$	366–424	549–578	368–388	549–577
GaI_3	446–472	$(693–706)^1$	466–472	693–706
$EkaSiCl_4$ ...	198–273	$(337–342)^2$	216–220	$(337–340)^2$
$EkaSiBr_4$ ...	295–303	426–429	266–275	426–429
$EkaSiI_4$ ...	393–404	563–568	393–404	564–565
$AsCl_3$	244–245	....	244–245	....
$SeCl_2$	229–243	337–388	230–243	383–388
$SeBr_2$	251–260	337–426	274–278	451–454
SeI_2	309–393	493–563	350–351	545–563
$ZrCl_4$	....	....	307–345	495–496
$ZrBr_4$	....	....	363–370	549–562
ZrI_4	....	....	441–469	677–685
$InCl_3$	346–446	540–586	377–377	549–569
$InBr_3$	424–677	592–637	408–408	608–622
InI_3	472–483	706–723	472–483	716–723
$SnCl_4$	239–270	....	239–270	....
$TeCl_2$	309–345	373–390	336–337	472–496
$TeBr_2$	345–363	390–549	345–363	530–537
TeI_2	383–438	549–622	428–428	620–622
BiI_3	554–555	836–893	554–555	836–893
$YtCl_3$	....	....	299–305	388–421 ⎫
$YtBr_3$	....	....	329–351	451–464 ⎬ 3
YtI_3	....	....	419–428	576–579 ⎭
$CeCl_4$	....	....	406–412	552–559 ⎫
$CeBr_4$	....	....	422–447	607–615 ⎬
CeI_4	....	....	508–522	733–737 ⎭
$LaCl_3$	....	....	384–387	505–513
$LaBr_3$	....	....	409–409	536–562
LaI_3	....	....	489–490	646–663
$TlCl_3$	....	....	477–477	....
$TlBr_3$	....	....	503–514	....
TlI_3	....	....	577–577	....
$PbCl_4$	....	....	323–354	475–521
$PbBr_4$	....	....	361–383	533–578
PbI_4	....	....	493–504	651–668

[1] Or (633–640).

[2] Mendeljeff predicts (Liebig's *Ann.* Suppl. 1870–72, p. 202) that Ekasilicon will boil somewhat below 373°.

[3] From this point onwards the values given are only rough approximations.

The melting-points and boiling-points which have been calculated for some of the substances cannot be determined in the ordinary way, as they undergo decomposition below their melting-point or boiling-point.

Confirmation of Results obtained by the above Method.—The results given in Table IX., though not previously printed*,

* Though not printed, they were given in a paper read before the Royal Society in June 1879, an abstract of which was published in the 'Proceedings' in the same year.

were calculated out early in 1877, and have not since been revised in any way. From 1877 to the present time the following melting- and boiling-points have been determined by various observers. On comparison it will be seen that, with the exception of the chloride and bromide of tellurium, these agree very well with the values calculated seven years ago.

	Calculated in 1877.	Found.	Authority.
Cu_2Br_2, m.p....	774–790	777	Carnelley and Williams, 1880.
CsCl, m.p.	below 959	904	,, ,, 1880.
$BeCl_2$, m.p. ...	820–870	858–890	Carnelley, 1879.
$BeBr_2$, m.p. ...	802–820	858–890	,, 1879.
$AsCl_3$, m.p. ...	244–245	Below 244	Henry, 1879.
$GaCl_3$, b.p......	496–499	487–492	Boisbaudran, 1881.
CCl_4, m.p.	253–276	Solidifies at 248°, and will therefore melt a few degrees above this temperature.	Regnault, *Mém. Acad. Sc.* xxvi. p. 658. This determination was unknown to me when the calculation was made.
$TeCl_2$ { m.p....	309–345	482	Carnelley and Williams, 1880.
{ b.p. ...	472–496	600	,, ,, 1880.
$TeBr_2$ { m.p....	345–363	553	,, ,, 1880.
{ b.p. ...	530–537	612	,, ,, 1880.

It is thought that the difference between the calculated and experimental values for the compounds of tellurium may possibly be due to the molecules having the constitution

$$\begin{array}{c} Te=Cl_2 \\ \| \\ Te=Cl_2 \end{array}$$

instead of $Te=Cl_2$. With the object of throwing light on this point, some vapour-density determinations of the halogen compounds of tellurium are in progress.

III. and IV. Application of Melting- and Boiling-points to the Classification and Determination of the Atomic Weights of the Elements.

The following example will show how a knowledge of the melting-point or boiling-point of the normal chloride, bromide, or iodide of any element may render considerable service in the determination of its atomic weight, or for ascertaining its position in the general classification. For this purpose we will take Ti. Now supposing Ti were a new element, and that its position and atomic weight were unknown; then, in order to determine these latter, we should have to find its equivalent and the melting-points and boiling-points (where possible) of its halogen compounds, and then to collect together

those *calculated* limits (see Table IX.) for little-known or undiscovered elements within which these lie, and we should obtain as follows:—

CHLORIDES.		BROMIDES.		IODIDES.	
M.P. of Titanium chloride not determined.	B.P. *found* for Titanium chloride =408°.	M.P. *found* for Titanium bromide =312°.	B.P. *found* for Titanium bromide =503°.	M.P. *found* for Titanium iodide =423°.	B.P. *found* for Titanium iodide =633°.
	B.P. *calculated* for the position usually assigned to $TiCl_4$ =(405–408°).	M.P. *calculated* for position usually assigned to $TiBr_4$ =(295–343°).	B.P. *calculated* for position usually assigned to $TiBr_4$ =(493–507°).	M.P. *calculated* for position usually assigned to TiI_4 =(414–442°).	B.P. *calculated* for position usually assigned to TiI_4 above 614°.
	Ditto for position usually assigned to $YtCl_3$ =(388–421°).	Ditto for position usually assigned to $YtCl_3$ =(329–351°).		Ditto for position usually assigned to $YtCl_3$ =(419–428°).	
				Ditto for position usually assigned to $EkaSnI_4$ =(428–490°).	Ditto for position usually assigned to $EkaSnI_4$ =(568–654°).

This table shows that Ti must occupy in the classification either the position assigned by Mendeljeff to the little investigated Yt (to the exclusion of this latter element), or that of the undiscovered element EkaSn, or, lastly, that which it really occupies; but it cannot belong to either of the first two positions, for neither do the experimental boiling-points of its bromide and iodide agree with those calculated for the first position, nor do the experimental melting-points and boiling-points of its chloride and bromide agree with those calculated for the second position; nor, again, does its equivalent agree with either of those which the first and second positions require. Consequently the only position which remains is that usually assigned to Ti; and this also agrees with its experimental equivalent.

Boisbaudran has found that gallium chloride melts at 348°·5. Taking this melting-point and the equivalent 23·3 as our only available data, and proceeding as described above in the case of Ti, we find that we must give to gallium the position of Eka-aluminium in Mendeljeff's table. This is the position actually assigned to it for other reasons by Boisbaudran.

There has recently been some dispute as to the atomic

weight of Be. From his determination of its specific heat, Emerson Reynolds (Phil. Mag. [5] iii. p. 38) concludes that its atomic weight is 9·2, and that it is a dyad; whilst Nilson and Pettersson (*Deut. chem. Ges. Ber.* xi. p. 381), also Humpidge (Phil. Trans.), from their determination of its specific heat, give to it the atomic weight 13·8, in which case it would be a triad. Now according to calculation the melting-points of its chloride, bromide, and iodide ought to be (820–870), (802–820), and (766–777) respectively if it has the atomic weight 9·2; and although these numbers are somewhat uncertain, from their having been calculated for an element of the second group (see Table IX.) occupying the position generally assigned to Be, yet they are sufficiently near in order to determine whether Be is really a dyad or a triad. If it be a dyad, the melting-points of its halogen compounds must be considerably higher than those of boron (see Conclusion V. p. 13, also Plate); whereas if it be trivalent, these melting-points must be comparatively low. If the metal is a dyad, the melting-point of its chloride should also be higher than that of the bromide, and the latter higher than that of the iodide; whereas if it be a triad, the reverse should be the case.

To throw light on this point, I determined as carefully as possible the melting-points of the chloride and bromide of beryllium, and found that the chloride fuses between the melting-points of $Ag_4P_2O_7$ (melting-point = 858°) and $NaPO_3$ (melting-point = 890°), thus agreeing with the number (820–870) calculated for $BeCl_2$ (Be = 9·2). The bromide also fuses between 858–890, and almost exactly at the same temperature as the chloride, but, if any thing, slightly higher, the calculated number for $BeBr_2$ being 802–820. The rather high number obtained for the bromide is probably due to the substance being so readily volatile below its melting-point, that the heat absorbed during its conversion into vapour cools the remainder of the solid, and thus prevents it melting so soon as it otherwise would do. $BeBr_2$, however, is much more easily volatile than $BeCl_2$. The chloride and bromide used for the determination of the melting-points were the pure compounds obtained by repeatedly distilling the crude substances, produced by passing chlorine and bromine respectively over a red-hot mixture of the oxide and charcoal.

An analysis of the chloride gave:—

	Found.	Calculated.
Be	11·93	11·47
Cl_2	88·90	88·53
	100·83	100·00

Now, judging from available data, the normal chlorides of all triad elements melt below 510° ($BiCl_3$ being the highest known, melting-point=503°), and their normal bromides below 500° ($BiBr_3$ being the highest known, melting-point= 480°). These results therefore confirm the view that beryllium is a dyad, with atomic weight 9·2. This is rendered still more evident by an inspection of the Plate, showing the curves of the melting-points of the halogen compounds of the elements[*].

FLUORIDES.

As fluorine is an *even*, whilst Cl, Br, and I are odd members of the seventh group, the fluorides cannot strictly be compared with chlorides, bromides, and iodides as regards their melting- and boiling-points. The melting-points and boiling-points of the fluorides, however, taken apart from those of the other halogens, appear (if we may judge from the few melting- points and boiling-points which are known) to obey laws similar to those which govern the melting-points and boiling- points of the chlorides, bromides, and iodides.

II. *On Salt-Solutions and Attached Water.*
By FREDERICK GUTHRIE [†].

VIII.

[The paragraphs are numbered in sequence with those of my memoir on Eutexia, *anteà*, vol. xvii. p. 462.]

§ 232. *INTRODUCTION.*—When, some ten years ago, the first experiments in this subject were brought before the Physical Society, it was pointed out that the key to the temperature of any salt-ice freezing-mixture was to be found in the temperature of fusion of the cryohydrate of that salt. Since then further light has been thrown upon the subject by the discoveries and observations of others. Thus, Ditté has obtained a hydrate (probably a subcryohydrate) of hydrochloric acid, and Wroblewski has obtained a similar hydrate of carbonic acid. Pettersson, in his exhaustive study of marine ice, made in the 'Vega' expedition, has explicitly admitted that the phenomena presented by freezing and frozen sea-water can only be satisfactorily explained by the formation and properties of the cryohydrates. Though this tacit corro-

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[*] Since writing the above, Messrs. Nilson and Pettersson (*Deut. chem. Ges. Ber.* xvii. p. 987) have determined the vapour-density of beryllium chloride, and find that it corresponds with the formula $BeCl_2$, and conse- quently that Be=9·2.

[†] Communicated by the Physical Society. Read May 24, 1884.

boration or explicit adoption by foreigners of the views I ventured to advance has given me perhaps more satisfaction than if they had been only accepted by English physicists, I may be allowed to express some regret that the latter do not yet appear to be awake to the interest and importance of the subject. It gives me, therefore, unusual pleasure to offer them this my eighth memoir on this branch of Molecular Physics.

In this memoir I shall first make a study of the ammonia group in its behaviour with water. I add a little to our knowledge of ammonia itself in this respect. Then are examined the effects of replacing one or more of the hydrogen equivalents by ethyl. Then will be described in some detail the behaviour with water of some aniline salts.

Secondly (§§ 249–255), I shall shift the region of my inquiry upwards on the thermometric scale, and include in it temperatures at which the solid fuses *per se*, and shall thus establish the continuity of the phenomena of fusion with those of solution, making clear the fact that certain bodies, originally solid, may at high temperatures become miscible with water in all proportions. It will be shown how this latter branch of the inquiry, apart from its purely physical interest, has a great geological one, as it throws light on the pyrohydration of igneous formations, just as the cryohydration in floes has thrown light on the formation of those masses.

§ 233. *Ammonia.*—Anhydrous ammonia, NH_3, according to Faraday becomes solid under a pressure of 20 atmospheres at a temperature of $-75°$ C. According to Fourcroy and Vauquelin, a perfectly saturated solution (? saturated at air-temperature) freezes between $-38°$ and $-41°$ C., forming shining flexible needles; at $-49°$ C. it freezes to a grey gelatinous mass.

Starting with a 33·3-per-cent. solution, I made solutions of various strengths, and found that pure ice separated from them at the following temperatures :—

TABLE XLV.

Showing Separation of Ice from Solution of Ammonia.

Per cent. of NH_3.	Per cent. of water.	Temperature of beginning solidification.	Body separated.
1	99	$-0°\!\cdot\!8$	Ice.
3	97	$-3\!\cdot\!2$	,,
5	95	$-5\!\cdot\!6$	,,
10	90	$-12\!\cdot\!8$	,,
15	85	$-21\!\cdot\!4$	,,
20	80	$-43\!\cdot\!4$	,,

Judging by the analogy, which will appear more clear in the sequel, it seems that the body mentioned by Fourcroy is a subcryohydrate, and that the gelatinous mass mentioned still contained too little water for the cryohydrate. I find that a 33·3-per-cent. solution does not crystallize at −80° C.; and I have as yet been unable to obtain the true cryohydrate.

§ 234. *Ethyl-Ammonias.*—The ammonias whose relationship to water have next to be described were obtained from Kahlbaum of Berlin. They were verified by means of their boiling-points, their platinum double chlorides, and by titration with standard hydrochloric acid. Those which I here employ were found to be pure.

§ 235. *Ethylamine.* Boils at 18° C.—The solutions of this base were made by dropping an indefinite quantity into a narrow-necked weighed bottle, putting in the stopper, weighing, surrounding by a freezing-mixture, and running in the proper quantity of distilled water from a burette. When the quantity of water was small, it was dropped in from a capillary tube until the proper weight was reached.

The first five solutions, namely those containing 0·99, 5, 10, 15, and 20 per cent. of ethyl-ammonia ($NH_2C_2H_5$), showed, on cooling, the separation of the easily recognizable ice-crystals. On further cooling the 20-per-cent. solution, the separating crystals became opaque, betraying the cryohydrate; this occurred at −13°·9, whereupon the temperature became stationary. After ten or twelve grams had solidified at −13°·9, the remaining liquid was poured into a fresh tube and reduced to the same temperature. The same operation having been performed three times, the liquid was considered pure; 3·589 grams of it were weighed in a stoppered bottle, diluted with water, over-neutralized with hydrochloric acid, evaporated in a water-bath in a platinum dish until the chloride became quite hard on cooling, heated to incipient volatilization, and weighed. There was thus obtained 1·3415 gram chloride of ethyl-ammonium or 0·7407 ethylamine, which corresponds to 20·64 per cent.

On cooling a stronger solution than this, solidification begins at a higher temperature, reaches a maximum between 30 and 35 per cent., and again falls, passing out of the range even of a solid carbonic-acid cryogen. As there is only one tenth of a degree difference between the points of initial solidification of the 30- and 35-per-cent. solutions, and guided by the general shape of the curve, I made a 32·4-per-cent. solution, and found that solidification began at −8° C.

It is well known that anhydrous ethylamine is not solidifiable in a solid carbonic-acid cryogen. Accordingly, the solid which

separates from an aqueous solution of ethylamine of any and every strength between −13°·9 and the anhydride is one of those remarkable bodies which I have called subcryohydrates, and which have been observed in the chloride and iodide of sodium.

The subcryohydrate of ethylamine, as a glance at the curve (fig. 1) will show, has a solidifying-point within certainly one tenth of a degree C. of −8°, and, as certainly, it has within two or three tenths of a per cent. the composition of 32·4 per cent. It is minutely crystalline, and of nearly the same specific gravity as the residual liquid. Its solution is eminently supersaturable, and in that state is curiously viscid. It is not easy to see a way whereby it might be made to purify itself in the act of formation. The existence of these solid hydrates of a substance which by itself resists solidification by a carbonic-acid cryogen, and the fact that their melting-points are only ten degrees or so below 0° C., is surely an unanswerable argument that they are not mere juxtapositions of independent crystals of the two constituents.

Any horizontal line between −13°·9 and −8° cuts the curve of aqueous ethylamine in three places. Within these limits, therefore, there are always three degrees of strength of the solution, which begin to solidify at the same temperature. Thus, if we find an aqueous solution of ethylamine begin to solidify at −12°, we do not know whether it is of the strength 18·7 or 22·2 or 43·3 per cent. Further, it may be noted that, on adding water of the air-temperature to the solid subcryohydrate, a depression of temperature occurs to a point lower than that at which the subcryohydrate stood.

TABLE XLVI.

Separation of Solids from Aqueous Solution of Ethylamine.

Per cent. of Ethylamine.	Per cent. of water.	Temperature at which solidification begins.	Nature of solid.
* 0·9901	99·01	− 0·4	Ice.
5	95	− 2·0	,,
10	90	− 4·7	,,
15	85	− 8·4	,,
20	80	−13·3	,,
20·64	79·36	−13·9	Cryohydrate.
25	75	− 9·5	Subcryohydrate.
30	70	− 8·1	,,
32·4	67·6	− 8·0	,,
35	65	− 8·2	,,
40	60	−10·1	,,
50	50	−16·4	,,

* Accidentally taken 1 to 100, instead of 1 to 99.

§ 236. *Diethylamine.*—Let us now replace another equivalent of hydrogen by the same organic radical, and examine the relation towards water of diethylamine, $NH(C_2H_5)_2$. This liquid boils at 54° (57°, Hofmann) at 31·02 B. The solutions were prepared precisely as in the preceding case.

The four weakest solutions, which contained 5, 10, 15, and 20 per cent. of base respectively, gave no trouble. But from this point the curve (fig. 1) descends very sharply towards the cryohydrate, and rises again with equal steepness. A 22-per-cent. solution yields ice on incipient solidification at 9°·9; while a solution containing only 1 per cent. more, a 23-per-cent. solution, yields subcryohydrate at the same temperature of 9°·9. To this difficulty has to be added the circumstance that I have not met with a substance which shows so extraordinary an aptitude for supersaturation. The solutions of the sub-cryohydrate in the anhydrous base (all those to the right of the cryohydrate in fig. 1) and the cryohydrate itself may be cooled to −20°, and diligently stirred without showing signs of solidification. The solidification may then be started by a cryogen of solid carbonic acid and ether. Moreover, the solutions near the saturated conditions are as viscid as glycerine; so that the appeal from one part of the liquid to another in the matter of crystallization, and consequent change of composition of the residual liquid, is tardy. These circumstances made it impossible to obtain the cryohydrate pure for analysis in the ordinary way by automatic purification. But they also made it unnecessary; for since a 22 per cent. gives up ice and a 23 per cent. gives up subcryohydrate at the same temperature (9°·9), it follows that a 22·5-per-cent solution must, within a probable error of about 0·2 per cent., have the composition of the cryohydrate. Having made such a solution, and cooled it to −10° in a salt-ice cryogen, the bottom of the tube containing it was dipped in a little carbonic-acid cryogen until a little white opaque regulus of crystals was formed. The whole being then restored to the ice-salt cryogen and stirred, opaque solidification began, the rounded tufts of crystals much resembling oatmeal in suspension. From first to last the temperature now remained constant at 11°·0 C. Of course there was no need to analyse a body thus synthesized.

TABLE XLVII.

Separation of Solids from Aqueous Solution of Diethylamine.

Per cent. of Diethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of solid.
5	95	$-1 \cdot 1$	Ice.
10	90	$2 \cdot 9$	,,
15	85	$5 \cdot 2$	,,
20	80	$8 \cdot 4$	,,
21	79	$9 \cdot 1$	,,
22	78	$9 \cdot 9$	,,
22·5 ($\pm 0 \cdot 2$)	77·5 ($\mp 0 \cdot 2$)	$11 \cdot 0$	Cryohydrate.
23	77	$9 \cdot 9$	Subcryohydrate.
25	75	$9 \cdot 1$	,,
30	70	$8 \cdot 3$	,,
35	65	$8 \cdot 0$	,, (pure)
40	60	$8 \cdot 2$	,,
45	55	$8 \cdot 6$	,,
50	50	$9 \cdot 1$	,,
60	40	$12 \cdot 2$	,,
70	30	$23 \cdot 4$	,,

Diethylamine does not solidify in a carbonic-acid cryogen.

§ 237. *Triethylamine*, $N(C_2H_5)_3$. Boils at 88°.—Viewed as an anhydride, we should expect, *à priori*, to find a greater difference between the physical properties of this body and those of diethylamine than between those of the latter body and ethylamine. Indeed, the difference might be expected to be comparable with that existing between the properties of ethylamine and those of ammonia ; for the replacement of the first and the last equivalent of hydrogen by ethyl would be expected to effect a difference of kind, while the replacement of two instead of one would effect rather an alteration in degree. Be this as it may, the properties of triethylamine in reference to water are quite exceptional, or at least very remarkable. The solutions of strengths 5, 10, and 15 per cent. yielded ice ; the latter and the 20 per cent. can be employed for obtaining the cryohydrate, but the 20 per cent. begins its solidification with the subcryohydrate. The solidifying temperature of the cryohydrate is −3°·8 C. This cryohydrate contains 19·15 of the anhydrous base. It may be remarked that the hydrochloride of this base retains hydrochloric acid with such firmness that, even when heated to incipient volatilization, it still remains acid *.

* A few grains of chloride of triethyl-ammonium heated on a hot spatula exhibit a beautiful phenomenon. The columns and whirls of white smoke can be watched petrifying in the air to white soot without much change of form.

The subcryohydrate of this body is, like those of the previously examined ones, very prone to supersaturation; so that, in examining the richer solutions, it is advisable to have recourse to the solids of previous preparations; which act like a ferment. A nearly remelted tubeful of the subcryohydrate, set to resolidify very slowly, crystallizes in bright laminæ one or two millimetres in diameter. More quickly frozen in repose, crystalline masses an inch long are fashioned upon the glass.

TABLE XLVIII.

Separation of Solids from Aqueous Solutions of Triethylamine.

Per cent. of Triethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of body formed.
5	95	$- 1 \cdot 0$	Ice.
10	90	$- 2 \cdot 0$	,,
15	85	$- 2 \cdot 9$	,,
18	82	$- 3 \cdot 4$	,,
19·1	80·9	$- 3 \cdot 8$	Cryohydrate.
20	80	$- 3 \cdot 5$	Subcryohydrate.
30	70	$- 4 \cdot 1$	,,
40	60	$- 5 \cdot 1$	,,
50	50	$- 6 \cdot 7$	,,
70	30	$-13 \cdot 6$	,,
80	20	$-20 \cdot 6$	,,

For the curve, see fig. 1, p. 31.

§ 238. Triethylamine is one of those rare bodies which, like sulphate of sodium, sulphate of calcium, caustic lime, and a few others, are more soluble in cold than in hot water. The behaviour of the three bodies named is clearly traceable to the decomposition by heat of definite hydrates. Without laying undue stress upon this, it seems that the phenomenon in question is one of decomposition, which so often follows increased temperature, and not an inversion of the rule that solubility also increases with temperature. The body decomposed in the case before us is clearly a hydrate—either the cryo- or subcryohydrate. Accordingly, though striking in its presentation, the phenomenon is really quite continuous with the decomposition by heat of oil of vitriol; which decomposition, I presume, does actually take place when that liquid is heated above its boiling-point (in a closed vessel). But while in the latter case the products of decomposition are probably miscible, and mix, though held apart from chemical union by heat-tension, with the hydrates of ethylamine the products of thermal decomposition are separated not only chemically but in mass, because, when chemically separated, they are not molecularly miscible, at least in all proportions.

The following table shows the temperatures at which turbidity begins and ceases in aqueous solutions of triethylamine of various strengths. (See also fig. 1, " Triethylamine and Water as liquids.")

TABLE XLIX.

Separation in Aqueous Solutions of Triethylamine.

Per cent. of Triethylamine.	Per cent. of water.	Critical temperature between clearness and turbidity.	Remarks.
1·96	98·04	78°	Becomes clouded, and begins to boil.
3·85	96·15	41	
5	95	34	
8	92	23·5	
10	90	21·3	
15	85	18·8	
18	82	18·6	
20	80	18·6	
30	70	18·2	
40	60	18·4	
46·46	53·54	18·3	
50	50	18·4	
70	30	17·1	
80	20	13·4	
90	10	6·1	
94·5	5·5	−7 (about)	
99	1	......	Complete liquid solubility at all temperatures.

A solution containing only 0·99 per cent., sealed in a very strong glass tube and heated to 200° C., did not show any opalescence.

A 1·96-per-cent. solution begins to give off bubbles of gas at the same temperature at which it becomes turbid. A still more dilute solution, namely a 0·99 per cent., does not become turbid at 200° C., when it is heated in a sealed tube. The curve (fig. 1, " Triethylamine and Water as liquids ") shows the relationship above examined. The following example illustrates the history of a solution. Ten grams of ethylamine and 90 grams of water, shaken together at 25°, form a white emulsion. On standing at that temperature, two transparent layers are formed, of which the upper is ethylamine saturated at 25° with water, and the lower water saturated at 25° with ethylamine. On heating to 28°, both layers become turbid ; the upper sheds water saturated at 28° with ethylamine, which falls, and the lower ethylamine saturated at 28° with water, which rises. These new quantities join their respective camps, the constitution of which has, of course, been altered by the

departures, and is now that of saturation at the new tempera-
ture in the two cases. The surface of demarcation shifts
towards the centre of the mass. Similar effects follow further
rises of temperature. Let now the tube cool. The former
condition is reestablished. On further cooling, the surface of
demarcation shifts—rises in this case as the two liquids mix
more with one another. At $21°\cdot3$ perfect solution ensues,
and this is well marked within a tenth of a degree. Just
above this temperature the mass is opalescent, just beneath it
it is perfectly limpid. When at this critical temperature, the
warmth of the hand only momentarily applied makes a wide
test-tube of the limpid mixture quite milky. Nor can such
a test-tube be passed so nimbly through a flame as not
to exhibit the same change. Following the temperature
downwards, we find the solution remains clear below $0°$, until
we reach $-2°$, whereupon crystals of ice appear. These
increase with the falling temperature until $-3°\cdot8$ temperature
and $10\cdot1$ per cent. is reached. The cryohydrate now solidifies,
and no further percentage change is possible; nor tempera-
ture change, until solidification is complete.

A 40-per-cent. ratio only shows perfect mixture at $18°\cdot4$.
It remains a mixture until $-5°\cdot1$, whereupon subcryohydrate
begins to appear in the solid form. Its quantity goes on in-
creasing with lowering temperature until $-20°\cdot6$ is reached:
this marks an 80-per-cent. solution. At still lower tempera-
tures no doubt the liquid becomes more enriched. If the
anhydrous liquid is unsolidifiable by cold, then the ordinate at
100 per cent. is asymptotic; but if, as is more likely, the liquid
is solidifiable, the remainder of the water and of the ethyl-
amine will unite to form some hydrate even lower than the
subcryohydrate at some very low but constant temperature.
An 80-per-cent. ratio at $-30°$ is thick with solid subcryo-
hydrate. Perfect liquefaction takes place at $-20°\cdot6$. The
liquid remains clear until $+12°$ is reached. At and above
$12°$ separation ensues, which increases with the increasing
temperature. The curve (fig. 1, "Triethylamine and Water
as liquids") is virtually a straight line between 15 per cent.
and 50 per cent. The deviations are probably errors of obser-
vation; and these errors of observation are certainly not due
to want of definition of the occurring and vanishing turbidity,
which is well marked within $0\cdot025$ of a degree. Nor are they
due to errors of original weighing or change during mani-
pulation; for the very flatness of the curve shows that a great
change of composition has little effect upon the temperature
of saturation. If they are indeed errors, they arise probably
from the collecting together of the opalescing globules into

clear drops which separate down, leaving the liquid above as clear as though it had been cleared by cold. The indication from a gradually ascending temperature is accordingly more to be relied on than one from a falling temperature.

When water is added to triethylamine, but little heat is evolved. A very small rise in temperature occurs when the 30-per-cent. mixture is made. The constituents should be brought to about 10°; and in the final experiment the thermometer and thin glass bulb, in which the mixture is effected, are to be previously warmed fully to the temperature at which

Fig. 1.

Triethylamine and Water as liquids

(b)

+10°

0   10%

−10

Ethylamine

Triethylamine

Diethylamine

Ammonia
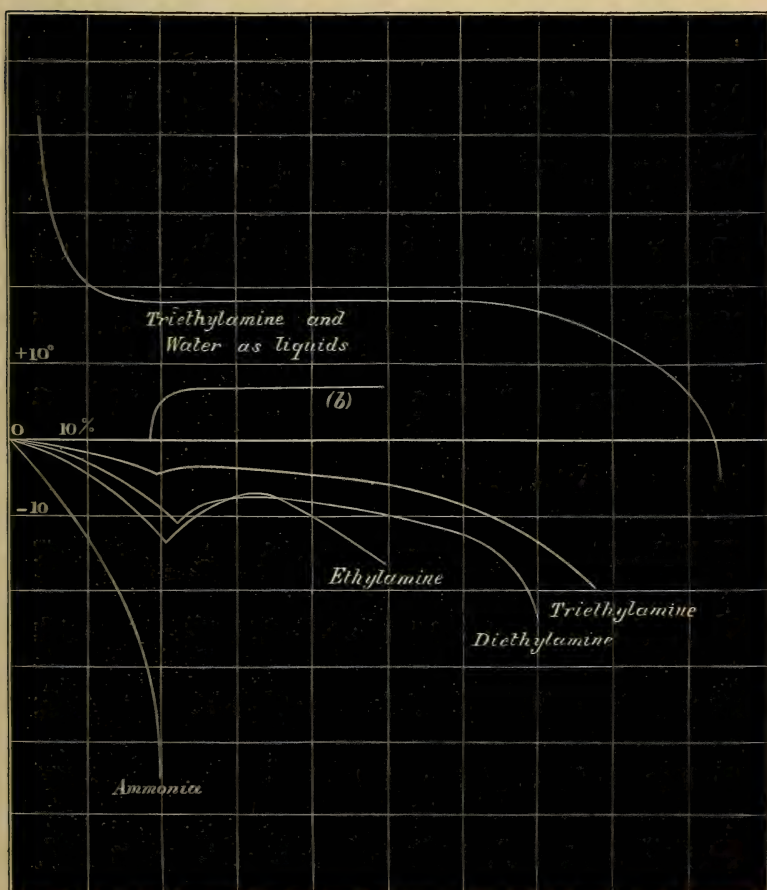
they stood at the end of the previous experiment. It is probable that the smallness of the heat of combination is nearly

connected with the ease of thermal separation. It is to be noticed, moreover, that in the region of the lower curve about the subcryohydrate, where the curve is flat because great change of *percentage* makes little difference in temperature of initial solidification, the curvature of the upper curve, fig. 1, "Triethylamine and Water as liquids," is also nearly nothing. Whether above or below zero, we are dealing apparently at every individual percentage with the same substance, the subcryohydrate : it is this region which is so keenly sensitive to changes of temperature.

§ 239. There is this important and essential difference between the genesis of a cryohydrate and that of a subcryohydrate. Solutions of nearly the cryohydrate strength approach the composition of that body as they lose heat and sink in temperature—weaker ones by the shedding of water (as ice), stronger ones by the shedding of salt or subcryohydrate. And this is true for all solutions from 0 per cent. up to the strength of the subcryohydrate; that is, on the curve, to the point where $\dfrac{dx}{dy}$ changes sign.

Not so with the subcryohydrate. A solution weaker than the subcryohydrate, to the left of it on the figure, will "run down" to the cryohydrate by dint of shedding the subcryohydrate. A solution stronger than the subcryohydrate will "run down" to the solidifying-point of the anhydrous liquid or to that of some secondary cryohydrate, no example of which is, I think, yet known. In either case, the liquid residue gets further and further away from the ratio in the subcryohydrate. The whole condition may be illustrated by the motion of a marble rolling upon the curve. It will run down to the bottom of the valley of the cryohydrate wherever it is placed on the slopes of that valley, and there remain in stable equilibrium. But placed upon the top of the great swell of the subcryohydrate, it will be at rest only if undisturbed, and so be in instable equilibrium. It will, if disturbed, either roll down to the bottom of the cryohydrate valley, or roll into the abyss of the anhydrous liquid. The cryohydrate is the level of a lake. The subcryohydrate is the watershed (subcryohydrate shed) of a hill-range.

The cryohydrate being an eutectic alloy, the subcryohydrate is a definite chemical combination, existing probably as such in the liquid when above zero, and liberating in its formation the heat observed when the two liquids are mixed; and as, for instance, sulphate of soda crystallizing either from an acid or alkaline solution leaves the liquid more acid or more alkaline than before, so the subcryo-

hydrate in its solidification leaves the liquid from which it separates continuously more aqueous or less aqueous according as it started from a solution more or less aqueous than itself. The " more " and " less," as here employed, refer of course to intensity, not to quantity, and the change is the analogue of that suffered by electricity when the surface of a conductor alters in size.

§ 240. *Some Applications of the above Property of Triethylamine.*—It appears from Table XLIX. that one weight of triethylamine with 19 weights of water is a ratio requiring 34° C., or 93°·5 F., that is a low blood-heat, to effect its turbidity. A ratio of 1 of ethylamine and 24·76 of water requires 41° C. or 105°·8 F. for the same effect to be produced: this is a fever heat. Accordingly, a few little glass capsules containing solutions of the triethylamine of strengths graduated between these two and thereabouts, and containing also a little mercury to assist the stirring-up when shaken, may be of use in the diagnosis of fever. The eye may be fastened to a thread or rod, and so introduced beneath the arm or into the cavities. I have made a series of 9 such capsules, which show turbidity at F.

68°·3, 69°·4, 76°·1, 79°·9, 91°·4, 98°·6, 105°·2, 111°·2, 123°·8.

§ 241. The radiation from an electric arc passing into an 8-per-cent. solution will warm it to opacity. Thin strips of variously coloured glass placed in such solutions will determine the opalescence after various time lapses,—the red glass acting the slowest, and the others, speaking broadly, the quicker the shorter the wave-length of the light they transmit. Two of complementary colour, which together absorb all radiation, or a single black one, act the quickest. Coloured glasses placed between the solution and the source of radiation cause opalescence in times which are the longer the shorter are the transmitted wave-lengths.

A few drops of the solution placed as a thin film between two thin sheets of flat glass, and prevented from evaporation by sulphur-cement around the edges, forms a sensitive plate. The hand placed upon it leaves a white silhouette. The spectrum thrown upon this plate leaves a transient record.

It is probable that the heat liberated when triethylamine is mixed with water is, if the expression may be allowed, the real image of the heat which on entering the mixture effects separation. They are both equal in quantity to the heat of subcryohydration; the former being that heat itself. It is a happy circumstance that the temperature at which separation begins within the limits of 20 to 50 per cent. solutions is a usual atmospheric temperature, namely 18°·3 C. (64°·94 F.).

§ 241 *a*. The quantitative relationship in respect to solubility existing between water and triethylamine was determined with considerable accuracy in the following manner. A 50 c. c. burette graduated to two-tenths was sealed at one end, and the mercury and water-meniscus values determined. It was drawn out to a narrow neck, and received about 2 c.c. of mercury. The whole being now counterpoised, a few c.c. of ethylamine were introduced, which proved to weigh 6·86 grams. A few grams of water were next added, the end sealed off and dried, and the whole reweighed. It was found that 7·885 grams of water were present.

The whole was now brought to a temperature low enough to ensure perfect mixture, and then gradually heated in a large beaker of water to which successive portions of warmer water were added. The water was diligently stirred. When the temperature is high enough to cause separation, the tube is kept at that constant temperature for half an hour, being repeatedly shaken. Taking the level of the mercury as constant, and calling it, when corrected for meniscus, 0, we have first the height of the plane of separation of the two liquids to read off. This requires no correction for meniscus at temperatures below 25° C. At 30° and 50° there is some + curvature (like water); this I have neglected. The height of the upper surface has to be read and corrected for meniscus. (For this the same correction is taken as for water.) The volume of water at 15° was 7·88 c. c., and the volume of triethylamine was 9·5 c. c. On bringing the two together, sufficient heat was set free by the mixture of part to prevent the mixture of the whole. On cooling to 15° the two mixed perfectly, and the volume was 16·6, showing therefore a contraction of 0·8 c. c. At 18°·3 the liquid still remained clear, but at 18°·7, that is in half a degree, a great separation had occurred. In the following table the corrected readings are given.

Separation between water and triethylamine (Triethylamine 46·45 per cent., Water 53·55 per cent.).

At °	Vol. of lower stratum.	Vol. of upper stratum.
15·0	0	16·6
18·3	0	16·6
18·7	3·5	13·2
19·0	4·5	12·2
20·0	6·1	11·4
21·0	6·8	10·1
22·0	7·2	9·7
25·0	7·8	9·3
30·0	7·9	9·4
50·0	8·0	9·7

So nearly complete is the separation at 25°, that above this temperature the upper stratum gives more in volume by expansion by heat than it loses by the rise of the plane of demarcation. To get an idea of the completeness of the separation at 50° C., we may compare the volume of the lower stratum at 50°, which is 8·0, with that of 7·885 grams of water at 50°, which is 7·93. This signifies that at 50° the lower stratum must be nearly pure water, and the upper nearly pure ethylamine. For the plane of separation stands only $\frac{1}{80}$ of the height of the original water-column above that height. See fig. 1, curve *b*.

[To be continued.]

III. *On the Electric Discharge in Gases.*
By Eilhard Wiedemann.[*]

[Plate II.]

IN a number of previous communications[†] I have investigated the behaviour of gases under the influence of electric discharges in various ways. The present research is a continuation of those investigations, and is concerned with (1) the effect upon the phenomena of interposing resistances between the poles of the machine and the electrodes of the discharge-tube ; (2) the phenomena obtained with different distances between the electrodes; (3) measurements of the heating effect upon the gas at different points of the discharge ; (4) deflection of the positive discharge ; (5) the behaviour of the discharge under the influence of the magnet; (6) the examination of an hypothesis as to the nature of the kathode-rays, as well as (7) the nature of the positive discharge and the stratifications ; (8) further observations on the influence of the magnet ; (9) behaviour of bad conductors as kathodes ; (10) connexion of the potential of the discharge with the form of the electrodes ; and (11) remarks on the management of electrophoric machines.

The great complexity of the problem explains why the separate phenomena have not been hitherto sharply distinguished from each other, as, for example, the " glow " appearing at somewhat higher pressures, the kathode-rays which are formed at lower pressures, &c.

There are also a series of interesting facts which have been clearly observed, but of many of which it was not possible for the same reason to determine the intimate connexion, by which remark it is of course not intended in any way to depreciate the work of the earlier investigators.

The separate details have only gradually become of importance, and even now it is often difficult to recognize them accurately in descriptions. I have endeavoured in the subjects of which I treat to distinguish these relationships as accurately as possible, and to make clear the conditions under which the phenomena occur.

In order to fix ideas we will agree upon the following nomenclature :—The phenomena are best observed in tubes having electrodes of a flat shape, because then the different stratifications are formed at right angles to the axis of the tube.

If k (fig. 3) is the kathode, scarcely any light is to be seen in the part of the tube next it—this we will call the *dark negative space*; next to this comes a stratification (b), sharply bounded on the side next the kathode, *the bright negative layer*. From it issues light ($b\,p$) towards the anode, which becomes continually fainter; this we will call the *glow-rays*. They are separated from the positive column of stratified light, of which the first layer is p, by a dark space $h\,p$ which may be called the *dividing space*. The whole is traversed by the kathode-rays $l\,m$ issuing from the kathode k.

1. *Influence of Interposed Resistances.*—The experiments were so arranged that the one pole of the electrophoric machine was connected with the earth, whilst the other was in connexion with one electrode of the tube, the other electrode being connected through the coils of a galvanometer with the earth. Resistances could be introduced either between the discharge-tube and the machine, or between the discharge-tube and the earth. They consisted of long glass tubes on the outside coated with shellac, and filled with distilled water in which conducting wires plunged. The discharge was observed in a mirror rotating with moderate velocity.

The result generally obtained was that, whether resistances were included or not, the deflection of the galvanometer was the same during uniform action of the machine, and that consequently the quantity of electricity passing through the discharge-tube in unit time was always the same.

The number of discharges, however, was found to be considerably greater when resistances were employed than without, and the same result was obtained at very different pressures. With discharge-tubes of the form usual to spectral-tubes the discharge is always discontinuous. With wider discharge-tubes

and flat electrodes, and when the gas has the density for which only a small potential is necessary for the discharge, the image in the mirror often appeared continuous when resistances were included, and, when they were removed, resolved itself into a series of separate images.

With discontinuous discharges, whether with or without included resistances, in both cases the result obtained * by G. Wiedemann and R. Rühlmann held good:—

"If the positive electrode is connected with the machine, and the negative put to earth, the number of discharges is always smaller than with the reverse mode of connexion ; the quantity of electricity necessary to bring about a discharge is therefore greater in the former case than in the latter."

It is a matter of indifference which of the two poles of the machine is positive and which negative. A reversal of the poles of the machine can always be produced by simply stopping the machine and starting it again.

The influence of the introduction of resistances may be explained as follows :—

To bring about a discharge from a metallic electrode, the electricity must be accumulated upon it with a perfectly definite density. If quantities of electricity are present upon conductors connected with the electrode, these may, when once the discharge has begun, and if they can reach the electrode quickly enough, leave the electrode at a smaller potential than is actually necessary for the commencement of the discharge. Such accumulated electricity is, however, present in the larger electrophoric machines in a high degree, and in the smaller machines in a smaller degree. To the conducting wires to the poles and to the combs of the machine and the neighbouring parts of the glass plates there are, between any two discharges, considerable quantities of electricity given off, which, as soon as discharge from an electrode has been established, flow to it and continue the discharge through the discharge-tube. If the connexions are metallic, the flow is much more rapid ; the time required to pass from the machine to the electrode is small in comparison with the definite, although immeasurably small, interval of time occupied by the discharge, and the whole quantity of electricity passes through at once. But at the same time the density upon the whole conducting system in connexion with the electrode sinks at once to zero ; and a longer time must elapse until it is again raised by the machine so high that a new discharge can take place. If we include larger resistances, the electricity will only flow slowly to the electrode when once the discharge has taken place. The

* Pogg. *Ann.* cxlv. pp. 235, 344 (1872).

density sinks therefore very rapidly at the electrode, and only small quantities of electricity can follow the first quantity. But the electricity accumulated upon the machine and flowing to the electrode will very soon raise the density to the necessary point for the discharge to take place again, and without large quantities of fresh electricity being produced. The number of the discharges must therefore in the latter case be much greater than in the first, with the same average intensity of current, since in the latter case, in each discharge only the quantity of electricity upon the electrode and close to it is discharged, and in the former, on the contrary, the quantity existing upon a much larger surface.

The machine itself therefore acts as a sort of feeble condenser.

But since the law relating to the difference between positive and negative electricity, discovered by my father, holds good both when resistances are included and without, his result cannot be explained by irregularities in the action of the machine, by different behaviour of the combs, and so on, since these would be compensated by the condensing action of the machine. We may call the discharge, when resistances are included, the *normal* discharge ; and the quantity of electricity which passes over, under the same circumstances, also the *normal* quantity, because it is just that quantity which, under the precise conditions of the experiment, must be accumulated on the electrode in order to bring about a discharge.

Since we observe, further, that always when, without resistances, the discharge is unstratified, it becomes stratified if resistances are included, we may also conclude that "*the stratified discharge corresponds to the normal discharge*;" and since the stratifications evidently require for their formation a regular discharge, it further follows that in the normal discharge the discharges occur in their simplest form.

In exact agreement with the above we find that, when once stratifications have been formed, whether with or without resistances, these disappear as soon as an air-spark is included, the quantity of electricity transmitted in each discharge being thus increased. Numerous experiments showed that, as a rule, the stratifications form best when the negative electrode is connected with the machine, and the positive with the earth through a large resistance. In the case of deviations of this rule, which certainly occur frequently, it was always found that the discharges, which were most numerous under the conditions noted, gave place to less numerous discharges. The reason of this could not, amongst numerous disturbing causes, always be certainly determined : thus, for example, very peculiar pheno-

mena occur when the machine is made to work very slowly, and consequently the supply of electricity is much reduced. If the pressure is so low that the dark negative space is about 2 centim. in breadth, whilst the glow-rays are separated from the positive discharge by the dividing space, or even if there is no positive discharge to be seen in the tube, and if then the machine is worked more and more slowly, the positive light expands round the positive electrode, whilst the negative light also expands considerably, until the positive and negative luminosities meet. This condition may be maintained for any length of time.

Since the experiments described above had shown that the discharges obtained simply from an electrophoric machine represent the simplest mode of discharge, it was necessary to investigate whether the propositions first stated by G. Wiedemann and R. Rühlmann [*] and myself [†] as to the independence of the heating of the gases upon the width of the tube, and the quantity of electricity traversing it, would also hold good for the case in which, by removing resistances, the quantity of electricity passing in each discharge is increased. If it is shown that changing the resistances produces no considerable effect upon the quantity of heat produced either in a wide or in a narrow tube, then it follows that if these two tubes are included in the same circuit, equal quantities of heat must be produced per unit of length, independent of the cross-section of the tube.

The experiments are arranged exactly like those described in a previous communication [‡]. In these experiments the whole quantity of heat produced and that evolved within the space connecting the electrodes (in the case of spectral tubes within the capillary part) were determined. Experiments on the heating of the electrodes themselves will follow later.

Let p denote the pressure, m W denote with included resistances, o W without resistances, F that no resistance but a spark 5 millim. long was included ; + or − that the positive or negative electrode of the machine, as the case may be, was connected with the tube, 0 that both were connected with the machine ; x as before denotes a very low pressure, and $x\,x$ a still lower pressure. The numbers under +, −, 0 are numbers which are proportional to the quantities of heat evolved in the unit time by equal currents. They represent here only the *relative,* not the absolute values.

* Pogg. *Ann.* cxlviii. pp. 35, 252 (1876).
† Wied. *Ann.* x. p. 202 (1880); Phil. Mag. vol. x. p. 357.
‡ *Ibid.*

Whole quantity of heat evolved.—The discharge-tube consisted of two small bulbs of 12 millim. diameter, connected by a capillary tube of 40 millim. length.

	$p=9.75.$			$p=1.9.$			$p=x.$		
	+	−	0	+	−	0	+	−	0
$m\,\mathrm{W}$ ...	...	...	2·92	3·11	3·08	...	7·33	6·59	
$o\,\mathrm{W}$ ...	...	...	3·27	3·52	3·23	3·43	8·36	6·86	6·54
F	...	...	10·10	5·0	5·08	...	12·31		

From these numbers we see that the total heating does not alter much, although a small increase is perceptible when the same electricity is transmitted in a decreasing number of discharges. The removal of resistances corresponds to the including of an air-spark, but the heating is certainly not greater in proportion to the smaller number of discharges. The same considerations which I have already stated[*] therefore hold good.

Heat evolved in the capillary connecting tube.

(1) Heating in a capillary of 1 millim. diameter :—

	$p=12.9.$		$p=2.$		$p=x.$		$p=xx.$	
	+	−	+	−	+	−	+	−
$m\,\mathrm{W}$ ...	10·8	13·0	4·5	5·35	2·52	1·90	2·0	1·46
$o\,\mathrm{W}$ ...	11·5	9·7	5·13	6·10	1·73	2·64	1·8	1·95
F	...	...	...	...	3·85	4·20	3·36	4·0

Here also the heating with and without resistances is nearly the same, and again the heating increases somewhat as the number of discharges decreases. This is pretty regularly the case when we consider only the negative discharges ; with the positive on the other hand, the minimum heating is at low pressures without a resistance. The positive discharge exhibits therefore here, as in many other cases, a less regular behaviour.

(2) Heating in a tube of 4 millim. diameter :—

	$p=12.7.$		$p=6.4,\ 5.9.$		$p=6.4,\ 5.9.$	
	+	−	+		−	
$m\,\mathrm{W}$ ...	...	...	3·5	...	6·4	
$o\,\mathrm{W}$ ...	8·3	11·1	4·5	...	6·4	6·3
F	...	...	...	6·8	...	9·0

* Wied. *Ann.* **xi.** p. 218 (1883).

$p = 0.8.$			$p = x.$	
	+	**—**	**+**	**—**
m W	1·6	1·6	0·6	0·8
o W	1·3	1·6	1·0	0·8
F	2·0	2·4	1·5	1·2

The result is here generally the same as with the narrower tubes. With a decreasing number of discharges the heating for equal quantities of electricity increases relatively very little. But if we take the numbers generally and observe that, especially at low pressures, the including of resistances increases the number of discharges immeasurably, we see that upon including resistances :—

(1) The evolution of heat in a gas by a given quantity of electricity which traverses it is almost independent of the circumstance whether it traverses in one discharge or in many.

(2) Hence, and from the previous result, it follows at once that with two tubes of different diameters, included one behind the other in the same circuit, equal quantities of heat per unit of length are evolved, whether the number of discharges be increased by inserting resistances or not.

In fact the amount of heating in the narrow and in the wide tubes is scarcely changed by the introduction of resistances; and since they are the same when no resistances are present, they must also be equal in the other cases. *Hence the same laws hold for the normal discharge as for that usually examined.*

In connexion with this the following remarks must be made. Certain advantages possessed by electrophoric machines over induction-coils and large galvanic batteries for the investigation of the discharge in vacuous tubes, have been noted by various observers, and in particular by my father and by myself. Our opinion is based upon the fact that, with the electrophoric machines, only the quantity of electricity is discharged each time which is required to produce the potential necessary, under the conditions existing in the tube and at the electrodes, to initiate the discharge.

That these views are not altogether correct is seen from the above; nevertheless for a number of investigations, and particularly for those of spectroscopic nature, electrophoric machines have advantages over other sources of electricity, not only over induction-coils but also galvanic batteries, since with these it is never possible to transmit large quantities of electricity in disruptive discharge without condensers, by the use of which the conditions are much complicated. With the elec-

trophoric machine the simple introduction of an air-spark is sufficient.

2. *Phenomena at different Distances of the Electrodes.*—It is of importance to be able to trace the phenomena which result when the distance of the kathode from the anode is changed within somewhat wide limits. It is essential that the vessel containing the electrodes should not be opened, for with each such opening the pressure would be altered : and the pressure under which the first determinations were made is, especially when low pressures are employed, not to be obtained again.

In order to carry out experiments in the direction indicated, I have constructed the following apparatus (Plate II. fig. 1) :—

A is the discharge-tube, which communicates with the air-pump at ϵ ; α is an electrode firmly melted in, which is connected with the machine in the manner already described[*]. A second electrode, insulated in the usual way, is inserted at δ ; the lower part has melted on to it the outer portion (e) of a ground glass joint. The inner portion (d) of the same forms one end of a U-tube, B C, whose longer limb B is about 900 millim. long, and its shorter limb C about 500 millim.; at the bend it is provided with a tap, and a platinum wire is melted in at E. The two portions of the joint are connected by caoutchouc bands at $s\,s'$ and $t\,t'$ in the manner already described[†]. So much mercury is next introduced into the U-tube that it stands in each limb about 400 millim. high.

The second electrode is formed by the plate β, which can be replaced by a point &c. It is fastened and connected with the machine as follows :—A thin platinum wire is melted into one end of a thin glass tube of suitable length, and the end within the glass tube covered with a little mercury. Into this dips the end of an aluminium wire which traverses the whole length of the tube, and on the top of which the plate is screwed. By this arrangement the whole conducting wire up to the electrode was covered with glass. In other cases the metallic wire was left uncovered.

The rod carrying the electrode thus floated with its lower end in the mercury in the limb B. By pouring mercury into C, or allowing it to run out from h, the level could be raised or lowered, and thus the electrode β made to approach or recede from the plate α. To regulate the motion it was necessary to provide the rod with some guidance: the simplest plan was apparently to make the tube B so narrow that the rod can just move up and down it ; there was, however, so powerful a capillary action, that not only in this case, but also when much

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[*] Wied. *Ann.* x. p. 206 (1880) ; Phil. Mag. vol. x. p. 360.
[†] *Ibid.* p. 209 (1880) ; Phil. Mag. vol. x. p. 362.

wider tubes were chosen and the rod came into contact with the sides of the tube, any regular motion was impossible. A star-shaped piece of platinum foil was therefore fastened to the lower part of the rod with a little wax; and as a further guide the upper end of d was covered with a plate having in it a hole just large enough to allow the rod to pass through. In order to introduce the electrode β into the space A, either the tube d was made larger than the plate, or else the tube A was cut in two; and after the plate had been introduced into A and the rod carrying it passed through C, the tube was melted together again; the terminal wires of the machine plunged in α and ϵ, or in α and δ, as the case might be.

In order to follow the rhythm of the discharges in the discharge-tube, which it is difficult to do in the luminous phenomena of the tube itself, on account of its great width, and especially when the discharges are irregular, or are confined to special parts of the tube, it is advisable, besides the wide tube, to include also a second tube in the circuit, which it is best to take of the form shown in fig. 2. This is made out of a wide tube by contracting the middle portion before the blowpipe; the tube is exhausted so far that it offers as small a resistance as possible to the current traversing it: a and b are flat electrodes which offer a smaller resistance to the currents than points do; they are placed as shown in the figure, in order to afford a rapid indication of the direction of the current. The middle portion of the tube is observed in the revolving mirror; its relatively great luminosity and small section render it easy to judge in the rotating mirror whether the discharges follow each other quickly or slowly.

In the following experiments it is always assumed that the exhaustion has been carried very far, so that the kathode is surrounded by a dark space :—

If we allow a positive electrode a (β of the figure) to approach a negative plate k (α of the figure), the positive electrode consisting of a wire which is cut off together with the glass surrounding it, and which dips into the mercury, the following phenomena are observed :—

If a is at a considerable distance from k we have a head of positive light about a, and stratifications between a and the glow-rays, of which even the first quite fills the section of the tube and is much curved. If a rises, the layers do not change their position, but one after the other disappear as soon as they touch the positive electrode; this is also the case with the last layer nearest the kathode.

As soon as the end of the wire has passed through this, there is only a small bundle of positive light to be seen upon

the end of the wire a; this also becomes smaller and smaller, without however entirely vanishing ; the positive light radiates upwards until the end of the positive electrode has broken through the boundary of the dark negative space about the kathode ; then it at once flows downwards like a small luminous waterfall. If the anode rises still higher and approaches the negative plate, the discharge ceases to issue from it and takes place, in highly inconstant fashion, between the upper surface of the mercury-column in the U-tube and k. I found thus, as Herr Goldstein has found, that if a positive electrode approaches a negative pole, the end of the positive column remains unchanged. But whilst he asserts that when the positive pole approaches the negative within a distance equal to or less than the interval between the negative pole and the first positive layer of the positive light, at the density employed the positive light disappears altogether, my often repeated experiments showed that there always remains on the positive electrode a little cap of reddish-yellow positive light even when the electrode has much over-passed the end of the positive light ; it becomes smaller only gradually. It seems as if this cap, adhering to the positive electrode, were firmly united to it.

Whilst the mode of combination of the positive and negative light can best be followed with electrodes of the form described, certain other phenomena appear much more distinctly if we employ a second plate for the movable positive electrode.

If we allow the anode to approach the kathode, all the phenomena are regular so long as the anode does not penetrate into the dark space about the kathode, *i. e.* layer after layer disappears, and when the last has been traversed there remains a small cap of positive light upon the plate, which ascends with it but becomes gradually smaller. If, however, the plate penetrates into the dark space, we always observe a deformation of the negative stratifications, the blue light is driven behind the kathode, whereas it was before only in front, and there forms on the wall a narrow strip of positive light, as also Hittorf [*] observed upon close approach of anode and kathode. The kathode-rays themselves, which usually proceed from the centre of the kathode, are compressed altogether to the edge of the kathode, from which they issue like a star, whilst the middle of the kathode remains quite dark [†] ; moreover kathode

* Pogg. *Ann.* vol. cxxxvi. pp. 1, 197 (1869).
† This experiment shows that the kathode-rays do not always run in the direction of the lines of force. In the case of two parallel plates the lines of force are at right angles to the plates, and in the space between them the potential falls most rapidly, nevertheless the kathode-rays issue from the edge of the plate.

and anode attract each other with great force. If they have been made to touch, and then we try to separate them, sparks leap across and the kathode vibrates to and fro.

If the machine works very slowly, then, as soon as the blue negative layer has been traversed, irregular discharges set in, the green light of which is seen at different points of the tube, just as with a tube which has been exhausted so far that the discharges traverse the gas only with difficulty.

A conclusion as to these last phenomena is furnished by experiments in which the poles of the machine are brought within a small distance, some 3 or 5 millim., of each other, and then the lower electrode is allowed to approach the other; as soon as the two electrodes are sufficiently near, a stream of sparks passes between the poles of the machine, whilst the tube remains dark. If, then, the distance of the electrodes is increased, the discharge in the tube suddenly commences, whilst no electricity passes between the poles of the machine. If, now, besides the experimental tube, we include also the comparison-tube in the circuit, then, when sparks are passing between the poles of the machine, we see the walls of the tube shine with bright green phosphorescence at the points where positive light appears in the ordinary passage of the discharge. The reason of this is, that the small distance between the plates of the principal discharge-tube causes this to act as a condenser; they become gradually charged until suddenly the discharge between the poles of the machine commences, and the whole quantity of (negative) electricity, which is accumulated on the one electrode of the tube, discharges itself suddenly backwards through the small tube, and thereby produces the green light.

It follows from the experiments described that, in highly exhausted spaces, the discharge between a positive and a negative electrode, if their distance apart is less than a certain limit, takes place with greater difficulty the nearer they are to each other. This result was confirmed and completed by the following experiment :—

Two discharge-tubes (figs. 4 and 4*b*) were connected at the same time with the pump, which in this case was a Geissler's pump, instead of the Töpler's pump usually employed. The tubes were each 26 millim. wide and 39 millim. long; electrodes of aluminium wire were melted into each, which were covered with glass except about 1 millim. In the tube *a* the electrodes were 1 millim., in the other tube *b*, 20 millim. apart; the tubes were included in parallel arc in the circuit of the machine. At high pressures the discharge took place only in *a*; at low pressures of about 5 millim. and less, in both tubes at the same

time, and at still higher exhaustion only in *a*. · When this was the case, if the mercury reservoir of the pump was raised, and the gas present in it thus driven again into the discharge-tubes, then the discharge took place again in *b* and not in *a*. This behaviour at high pressures, and at medium pressures, follows at once from the views ordinarily held : at high pressures the induction exerted by the electrodes upon each other, and on the layer of gas between them, is of importance ; at medium pressures the resistance of the positive column of light disappears in comparison with that of the negative light ; in fact, at medium pressures the two tubes differ only by having a positive column of different length, which exerts no perceptible influence upon the potential which is necessary to the discharge, so that the discharge can take place in both tubes at the same time. At the third pressure mentioned above, the dark space surrounding the kathode has, in the tube in which the electrodes are close together, spread out so far that it completely surrounds the anode. This opposes so great a resistance to the passage of the electricity, that the discharge traverses only the tube in which the electrodes are far apart, in which the dark kathode-space does not yet reach the positive electrode. Upon still further exhaustion the dark kathode-space surrounds the anode also in the tube *b*; and now the discharge must of course take place more easily in the tube in which the electrodes are near each other, since here there is a smaller part of the dark space to be traversed.

From the experiments described above we draw the following two important conclusions :—

(1) *The dark kathode-space opposes a very great resistance to the positive discharge.*

(2) *The union of the positive and negative electricities takes place in the " glow-rays."*

Hittorf[*] had already concluded, from experiments with electrodes near together, that resistances existed in the neighbourhood of the kathode; but since he did not vary the distance of the electrodes from each other, he was not able to determine the position of the resistance, so as to explain the phenomena.

3. *Heating of the Gas at different Distances from the Kathode.*—A whole series of experiments was undertaken, in order to investigate the decrease of heating-effect in passing from the negative pole towards the positive.

For this purpose a method was employed which has already been used by G. Wiedemann and R. Rühlmann [†] for another purpose. The junction of a thermo-electric element, consisting

* Pogg. *Ann.* cxxxvi. pp. 1, 197 (1869).
† Pogg. *Ann.* xlv. p. 35 (1872).

of two wires of iron and German-silver soldered together, was kept in contact with the outside of the tube by means of a spring, and the deflections read off upon an astatic galvanometer. These give a measure for the heating of the glass tube; and this is nearly proportional to the heating of the portions of gas close at hand. The experiments were always so arranged that the thermo-electric element was moved from the electrode towards the positive light, and back again in the opposite direction; the deflections were only noted after they had become constant.

In the following tables we give the differences of the deflections A observed at the position of the positive light, and at different distances E from the kathode. The length of the dark kathode-space was taken as measuring the pressure. In the curves the abscissæ represent the distances from the kathode, and the ordinates the deflections of the galvanometer.

I. A first series of experiments was made with a thin-walled glass tube 25 millim. wide; the electrodes were circular plates (fig. 5).

Exhaustion high. Dark space 37 millim. Green light faintly visible. Limit of positive light 210 (curve *a*).

E.	A.	E.	A.	E.	A.
0	27	60	22	210	9
13	20	90	23	250	3
32	17	122	22	290	0
42	17	160	18		

Dark space 30 millim. No green light. Limit of positive light at 220 (curve *b*).

E.	A.	E.	A.	E.	A.
0	19	70	23	190	9
11	17	108	20	220	3
32	17	160	13	280	0

Dark space 20 millim. No green light. Limit of positive light at 200 (curve *c*).

E.	A.	E.	A.	E.	A.
0	23	70	18	140	5
20	17	95	13	200	4
32	19	105	10	280	0
48	17				

Dark space 14 millim. Limit of positive light at 120 (curve *d*).

E.	A.	E.	A.	E.	A.
0	26	40	12	150	1
14	22	62	8	260	0
22	20	100	2		

Dark space 8 millim. Positive light begins at about 75 (curve *e*).

E.	A.	E.	A.	E.	A.
0	17	52	2	111	1
8	11	75	1	125	0
26	6				

II. Narrower tube 18 millim. wide (fig. 6).

Dark space 14 millim. Green phosphorescent light appeared even at the edge of the dark space, which, however, cannot be produced by the kathode-rays, since these issue from only a small portion of the kathode, and form a very slightly divergent pencil of rays, which at a distance of 14 millim. certainly does not meet the walls of the tube.

The boundary between positive and negative light cannot be determined. Also there are no stratifications. Fig. 6 *f* gives again the results obtained. The horizontal dimensions are in this diagram twice as great, and the vertical dimensions half as great as in the former ones.

E.	A.	E.	A.	E.	A.
0	38	44	95	130	11
8	47	65	66	170	3
14	71	100	25	222	0
30	100				

Dark space about 10 millim. (curve *g*).

E.	A.	E.	A.	E.	A.
0	51	40	112	130	11
10	71	60	86	180	2
16	92	100	32	220	0
22	102				

Dark space 8 millim. Discharge not stratified (curve *h*).

E.	A.	E.	A.	E.	A.
0	35	25	40	85	0
4	32	40	21	120	0
12	42	65	5		

Dark space 4 millim.

E.	A.	E.	A.	E.	A.
10	13	20	7	125	0
5	15	70	2		

The curves and numbers belonging to this second tube run exactly similarly to those found for the first tube.

III. Still narrower tube, 11 millim. wide.

Dark space 11 millim.

E.	A.	E.	A.	E.	A.
0	37	25	53	110	4
6	43	66	20	190	0
10	55				

Dark space 8 millim.

E.	A.	E.	A.	E.	A.
0	39	23	29	70	9
6	44	33	22	110	3
13	39	55	7		

Dark space 6 millim.

E.	A.	E.	A.	E.	A.
0	16	18	19	80	5
6	21	40	7	150	0

Dark space 3 millim.

E.	A.	E.	A.	E.	A.
0	22	15	9	120	0
2	19	65	6		

As with this tube the numbers run exactly as with the others, no curve is given.

All these experiments show that for the low pressures at which the dark kathode space is distinctly formed the following holds good :—

The production of heat in the electric discharge, starting from the positive electrode, rises at first slowly, then rapidly, reaching its maximum within the " glow-rays," from which point it decreases, attaining a relative minimum within the dark space about the kathode, to which, however, corresponds a much higher production of heat than in the positive light. At the kathode itself the production of heat attains a very high value, as shown by separate experiments.

If the pressure is increased, then with decrease of length of the dark kathode-space and shortening of the glow-rays the maximum and minimum of heating-effect move closer together, until at last they can no longer be separated by experimental means.

In order further to prove the peculiar course of the heating-effects obtained by the methods described and shown by means of the curves, the following arrangement was employed. At the upper end of the usual float carrying the electrode (Pl. II. fig. 1) a thermometer was attached, having its scale below, as shown in fig. 7. The mercury reservoir a is cylindrical, 5 millim. broad and 17 millim. long. It is protected against the kathode-rays by a horizontal screen b of mica carried by a pair of platinum wires c. But as these measurements are concerned, not with the temperatures of the gas, but with the quantities of heat produced in the unit time, the rise in temperature in equal times must be observed when the thermometer is placed at different points of the tube. We must, of course, also apply corrections for radiation and conduction : this was done by observations before and after breaking the current in the usual way. The measurements were carried out with a tube of about 140 millim. width and 500 millim. long. The dark space had a length of about 35 millim.

The following table gives the numbers found in three series (I., II., III.) of experiments. The different series are not comparable with each other as to absolute value.

E denotes the distance of the electrode ; W the observed rise in temperature in arbitrary units (generally $\frac{1}{1000}°$ per minute for a current producing 100 millim. deflection).

I.		II.		III.	
E.	W.	E.	W.	E.	W.
170	68	160	100	170	60
135	72	130	112	40	125
85	93	82	110	20	40
55	78	60	100	10	48
32	73	30	62		
20	45	14	20		
11	45				
5	54				

When the mica shield touched the electrode, a very great rise was observed.

The course of production of heat, as given by measurements with the thermometer, is thus exactly the same as that furnished by measurements with the thermo-electric element. From a minimum in the positive discharge it rises to a maximum, then sinks to a minimum, finally attaining a second maximum at the kathode itself.

The causes of these peculiarities in heating-effect cannot be determined without further experiment, but in the meantime we may note the following points.

The following equation holds good for any body traversed by the current

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -4\pi\rho,$$

where V denotes the potential at any point and ρ the density at the same point. If we have a tube (whose axis is the axis of x) which the current fills uniformly, then

$$\frac{\partial^2 V}{\partial y^2} = \frac{\partial^2 V}{\partial z^2} = 0; \text{ consequently } \frac{\partial^2 V}{\partial x^2} = -4\pi\rho.$$

In ordinary conductors $\rho = 0$: hence $\frac{\partial V}{\partial x}$ is constant, or, for unit length, $V_0 - V_1 = $ constant, being proportional to the resistance w. Hence if a denote an absolute constant,

$$V_0 - V_1 = aw,$$

Hence, with equal resistances, there must be equal productions of heat in equal lengths. If we find that the heat-production at different points of a tube is not constant, this is explained, if $\rho = 0$, by the fact that the resistance at different points of the tube is very different.

We have seen that close to the electrode we have a very

large production of heat, and that this decreases, reaching a minimum within the dark kathode-space, then it rises again to a maximum within the glow-rays, and sinks again towards the positive light.

It is therefore, according to our previous experiments, not possible to deduce the change in heating-effect from the change in resistance. We have not the maximum heating exactly at those places where the greatest resistance is offered to the radiation of the positive light. There are now two things possible, either (1) ρ is not zero—that is, free electricity moves within the tube ; or (2) a part of the fall in potential is used up at those points where the heating-effect is a minimum in imparting to the electricity a certain kinetic energy, which disappears again at the points of maximum heating-effect.

I shall endeavour to determine which of these two views is the correct one by special measurements of potential within the tube.

4. *Deflection of the Positive Column of Light.*—Two circumstances are of importance in connexion with the deflection of the sensitive positive light, which takes place upon touching the tube traversed by the discharge with the finger ; it sometimes consists in an irregular attraction, sometimes in a symmetrical deflection.

The one circumstance is the change in the distribution of free electricity upon the wall of the glass tube, by which the potential is lowered at the point touched, and the discharge is deflected towards the point touched ; this is especially the case at high pressures. The second circumstance is the formation of a dark space at the point where positive electricity flows into a conductor, or becomes bound. The experiments with the floating electrode show, indeed, that the passage of the positive electricity through the dark space meets with great resistance, and then the discharge bends round backwards. But so soon as any point of the wall is put into connexion with the ground, a kathode is produced at that point, kathode-rays issue from it, and the peculiar reddish light is seen ; consequently a dark space must form around this point, which prevents a portion of the tube from being traversed by the positive light, round which the discharge therefore bends.

Exactly similar reasons explain the luminosity of the tube when, the discharge being such that the tube remains dark, it is encircled by the fingers, or by a ring of tin-foil. Then the whole wall at the points touched becomes a kathode, and opposes to the discharge a great resistance, which is, of course, attended by a loss of energy, and has for consequence

a brighter luminosity of the gas. To the same cause I should be disposed to refer the great heating, otherwise so remarkable, in a calorimeter surrounding the discharge-tube, when a powerful discharge is sent through, and a good conducting fluid in connexion with the earth is employed in the calorimeter. The quantities of electricity, which become bound, become greater, especially where air-sparks are included, and consequently the formation of the dark space is much facilitated, so that the resistance offered to the passage of the discharge must increase in a high degree.

5. *Influence of a powerful Magnet upon the Discharge.*—The results which we have obtained also explain the phenomena which take place when the discharge is subjected to the action of a powerful magnet. The best form of magnet to employ is a cylindrical magnet, magnetized by a spiral of wire. It is known that under the influence of such a magnet the positive light is thrown into curves, which correspond nearly to those assumed by a solid flexible conductor fixed at both ends, whilst the glow-rays behave like a conductor fixed at one end. In a wide, strongly exhausted tube the stratified discharge was obtained, and then one pole of the electro-magnet described was moved along gradually from the positive pole-plate *a*. The well-known forms appeared in the positive light; the discharge appeared continuous in the revolving mirror. If we bring the magnet nearer to the negative pole, the glow-rays become compressed at the side, as may be seen from the green light which appears along the wall, and the positive light with its stratifications is seen to move, somewhat deformed it is true, in the space vacated by the glow-rays. The form of the discharge is represented in fig. 8. The bend at *b* corresponds to the magnet beneath.

If the magnet is brought still nearer to the kathode, and so far that the tongue *a* reaches to the limit of the dark kathode-space, it suddenly falls down and unites with glow-rays at the point where they strike the wall, and the discharges become discontinuous; so that in this case a much higher potential is necessary for the discharge than in the first case, or a considerable resistance is produced.

These experiments appear to me to show that the formation and position of the positive light does not depend so much on the position of the positive and negative poles, but rather upon the formation of the glow-rays issuing from the negative pole, and that generally, in accordance with their formation and position, the discharge shows a greater or less degree of discontinuity.

The above observation of the transformation of the con-

tinuous form of discharge into the discontinuous agrees entirely with the results previously obtained by approaching the positive to the negative pole. If we denote as the positive direction of the glow-rays that which issues from the bright kathode-layer, many discharges occurred so long as a union of the positive electricity could take place in the negative direction with the glow-rays; but as soon as that was no longer the case, much fewer discharges occurred. Exactly the same is the case here, so long as the glow-rays have not all been deflected from the axis of the tube to the side; the positive light can still unite with them in the negative direction. But as soon as a complete deflection has taken place, we have exactly the same case as if the positive electrode were behind the bright kathode-layer, and the discharge becomes continuous.

[To be continued.]

IV. *On Molecular Latent Heat.*
By Frederick Trouton, *Trinity College, Dublin*.*

ON comparing the quantities of heat necessary to evaporate at constant pressure quantities of different liquids taken in the ratio of their molecular weights, it is found that the amount of heat required by any body is approximately proportional to its absolute temperature at the point of ebullition. For example, the latent heat of bromine is 45·9, it boils at 63°, and the density of the body is 79·75. The latent heat of butyric acid is 114·7, it boils at 162°, and its density is 44. The quantities of heat required to evaporate quantities of the bodies in the ratio of their molecular weights is obtained by multiplying the latent heat by the density; and the quantities thus obtained have an approximately constant ratio to the absolute temperatures of the boiling-points, thus :—

$$\frac{45\cdot9\times79\cdot75}{273+63^\circ}=10\cdot89, \quad \frac{114\cdot6\times44}{273+162^\circ}=11\cdot59.$$

This ratio is nearly constant for most bodies, but is still more nearly so for those bodies which are chemically related to each other.

The relation, then, may be put into this simple form. The molecules of chemically related bodies, in changing from the gaseous to the liquid state at the same pressure, disengage quantities of heat, which may be called the molecular-latent heat, directly proportional to the absolute temperature of the point of ebullition. The similarity is very striking

* Communicated by the Author.

between this statement and Dulong and Petit's law, namely that the specific heat multiplied by the atomic weight is a constant quantity.

The following alcohols form a fairly well-defined class, with which perhaps water may be placed:—

	I.	II.	III.	IV.
Water	537	9	100°	12·95
Methyl alcohol...	263·7	16	55	12·86
Ethyl alcohol ...	202	23	79·7	13·17
Amyl alcohol ...	121	44	134	13·08
Cetyl alcohol ...	58·7	121	350	11·40

In column I. are arranged the latent heats, in column II. the densities, in column III. the boiling-points of the bodies ; and in column IV. are the products of the latent heat by the density divided by the absolute temperature of the boiling-point.

In the case of the following acids the theoretic densities of the first two are too small, owing to the vapour-densities being abnormally great at temperatures approaching the boiling-point. This is corrected for in formic acid in the ratio of 2·68 to 1·62, and acetic acid in the ratio of 3·19 to 2·08. Without the correction the numbers in the fourth column would be for formic acid 7·44, for acetic acid 7·86.

	I.	II.	III.	IV.
Formic acid	120·7	23	100°	12·31
Acetic acid	101·9	30	116	12·05
Butyric acid	114·7	44	162	11·59
Valeric acid	103·5	51	175	11·78

The following are the ratios in the case of a few methyl and ethyl salts:—

	I.	II.	III.	IV.
Methyl iodide ...	46·1	71	42°	10·38
Ethyl iodide......	46·9	78	72	10·59

	I.	II.	III.	IV.
Methyl formate...	117·1	30	33°	11·48
Ethyl formate ...	105·3	37	55	11·88

	I.	II.	III.	IV.
Methyl acetate ...	110·2	37	59°	12·27
Ethyl acetate......	99·0	44	75	12·45

The constant appears to be the same for the following bodies containing chlorine:—

	I.	II.	III.	IV.
Ethyl chloride	93	32·25	10°	10·59
Chloroform	61	59·75	62	10·87
Carbon tetrachloride ...	47	77·00	78	10·31
Phosphorus trichloride...	51	68·75	73·8	10·75
Arsenic chloride	46	90·75	132	10·30
Stannic chloride	30·5	130·00	114	10·24

In the case of phosphorus trichloride, as above for acetic acid, a correction must be made, for a similar reason, in the ratio of 5·0 to 4·7. Without this correction the number would be 10·11.

	I.	II.	III.	IV.
Sulphur dioxide	94·5	32	−10°	11·49
Carbon disulphide	86·7	38	+43	10·42
Ethyl oxide	91·1	37	34	10·97
Amyl oxide	69·4	79	176	12·20
Acetone.....................	129·7	29	56·3	11·42
Benzene.................. ...	94·2	39	80	10·40
Methyl butyrate	87·3	51	101	11·90
Turpentine	68·7	68	161	10·76
Ethyl oxalate	72·7	73	184	11·61
Bromine	45·9	80	63	10·89
Iodine	23·9	127	200	6·41

Iodine so far seems to deviate most from the above relation; but perhaps, owing to the nature of the body in question, the determination of the latent heat by Favre and Silbermann[*], as given in this table, need not be considered final. It would appear that experiments have only once been undertaken with a view to determine the latent heat of iodine. In fact even the boiling-point 200° is only approximate.

V. *On a "Speed Indicator" for Ships' Propellors.* By Sir ARCHIBALD CAMPBELL of Blythswood *and* W. T. GOOLDEN[†].

[Plate IV.]

IN February of last year, when visiting one of H.M. Dockyards, it was pointed out to us that a very urgent need was felt of some means of indicating with certainty the speed of naval engines, especially in ships carrying twin-screws, where the engines are not only distinct, but separated from each other by iron bulk-heads which prevent any communication between the two engine-rooms. The authorities intimated also that it was desired that several indications should be made simultaneously in various parts of the ship, and that the apparatus should be as far as possible automatic, and require no trouble or attention.

There are at present one or two instruments in existence for this purpose, but their indications are found to be untrustworthy when at sea; and we were warned that no instrument in which the force of gravitation played a part would be likely to receive any attention at the Admiralty. This consideration excludes the use of ball-governors or of any device depending on the weight of a fluid column; and led us to consider whether the desired conditions could not be fulfilled by a purely mechanical arrangement founded on the ordinary equation involving angular velocity,

$$v = r\omega.$$

It was at first difficult to see how this principle could be applied to a direct measure of ω, as no simple means are known whereby the variation in the velocity v of a point moving in a straight or curved path can be continuously measured. But it was soon apparent that the variable angular velocity ω of a body A can be compared with the constant

[*] *Annales de Chimie et de Physique* (3) xxxvii. p. 469.
[†] Communicated by the Physical Society. Read May 24, 1884.

angular velocity ω' of another body B, if a point on B at a distance r' from its axis of rotation has the same linear velocity as a point on the circumference of A. We then get

$$\omega = \frac{\omega'}{r}\ r',$$

in which $\frac{\omega'}{r}$ is constant, and thus ω varies as r'.

The condition is evidently satisfied by a disk pressing on the surface of a cone revolving at a uniform speed ; for the linear velocity of the point in the perimeter of the disk which is in contact with the cone, being identical with that of the corresponding point of the cone, will be proportional to the radius of the corresponding circular section of the cone, and consequently to the distance of the point of contact from the apex of the cone. If, further, the disk forms the nut of a screw rotating in the opposite direction to the cone, and the axis of the screw is placed parallel to the side of the cone, it is obvious that the nut and screw must have the same angular velocity for the nut to be at rest on the screw ; and the disk will therefore take up a different position on the screw as the velocity of the latter changes in value.

In the " Blythswood Speed Indicator " the screw is driven by the engine or shaft whose speed is to be indicated, while the cone has a constant speed communicated to it by clockwork. A scale placed under the screw shows the speed of the nut and screw when the nut is at rest ; and by a series of electric contact-pieces attached to a cable, the indications can be transferred to dials placed at any distance from the machine.

When the engines reverse, a clutch keeps the screw revolving always in the same direction, and at the same time pulls over a commutator placed in the electric circuit, so that the dials show not only the speed, but also the direction of motion, ahead or astern.

The clock is wound by the engine, and stops when the machinery is at rest ; and having a carefully balanced friction-governor, it is independent of gravity, and therefore keeps its time under all conditions of wind and weather.

We propose to add to the instrument a drum carrying prepared paper, upon which as it revolves a pencil will continuously trace the position of the nut, and thus keep a record of the performance of the engine for future reference.

The same principle can evidently be applied to a comparison of the speeds of two engines or rotating shafts, where both

are variable, if one drives the cone and the other the screw,

for $\dfrac{\omega}{\omega^l} = \dfrac{r^l}{r}$, in which r is constant.

We desire in conclusion to express the obligation we are under to Mr. Hilger for the admirable skill and patient intelligence with which he has successfully carried out our idea.

VI. *The Gas-Engine Indicator-Diagram.* *By* Professors
W. E. AYRTON, *F.R.S., and* JOHN PERRY, *M.E.**

[Plate III.]

THE members of this Society are probably aware that gas-engines are now largely in use, and that their use is still extending rapidly. There can be no doubt that gas-engines would be largely used, even if they were wasteful of fuel, on account of their being always ready to start or stop, and their requiring so little attention; but it is gradually becoming clearer that even small specimens of this kind of engine, whose history is merely beginning, are in actual fact less wasteful of fuel than the largest and most carefully constructed steam-engines. It is, for example, a demonstrated fact that, with a Dowson's generator not larger than the boiler used in the corresponding steam-engine, an Otto engine uses only 1·1 lb. of coal per indicated horse-power per hour. It is therefore not unreasonable to suppose that gas-engines will soon be employed even in the propulsion of ships.

The rapid growth of this new application of science renders it necessary that help should be given to practical men to enable them to use such observations as they are constantly making. This paper is intended to teach such men a *method* of obtaining information from the indicator-diagram of a gas-engine.

2. *The Action in the Otto Gas-Engine.*—This large model which we exhibit has been constructed in the workshop of the Finsbury College, to enable students to follow the motions of different parts of the gas-engine. It will be seen that when the piston is at the end of its stroke, only what we call the clearance-space behind it is filled with fluid. This fluid is a mixture of carbonic acid, water-vapour, and nitrogen, whose temperature is about 410° C.†, if there was an immediately

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* Communicated by the Physical Society. Read April 26, 1884.
† In our own observations at Finsbury we have not used any specially contrived apparatus, as our investigations were really for the purpose of

previous explosion. The temperature of the clearance-space fluid may be anything between 410° C. and the temperature of the atmosphere, depending on how recently an explosion has taken place. As the piston moves forward it draws into the space a mixture of gas and air. At the end of the forward stroke the pressure of the mixed fluid is nearly that of the atmosphere; in the back stroke the fluid is compressed. At the beginning of the next forward stroke the fluid is ignited, and rapid development of heat results, causing great increase in pressure, the pressure gradually diminishing until, just before the end of the forward stroke, the fluid is allowed to escape. In the next back stroke the piston drives the fluid out of the cylinder with the exception of what remains in the clearance, and thus completes a cycle of operations. In fig. 1 (Pl. III.) indicator-diagrams show the nature of the alterations in pressure and volume going on during the compression and working parts of the cycle; distances measured from O L representing pressure in pounds per square inch from vacuum, and distances measured from O P representing volume of the fluid, the unit of volume being the volume described by the piston moving through one foot of the length of the cylinder.

Four different diagrams are given whose compression parts practically coincide, the differences in their ignition parts being due to differences in the amounts of gas supplied. We have not thought it necessary to give a complete diagram in which the dismission and suction parts of the cycle should be represented.

The shape of the diagram is materially modified by the recentness of the last explosion, as this affects the temperature of the fluid before compression, and so modifies the actual amount of the mixture of gas and air entering the cylinder. To a less degree the shape of the diagram is affected in the discharge part of the cycle by the recentness of an explosion, as a recent explosion will have given the exhaust passages a higher temperature.

3. *The Nature of the Working Fluid.*—For the purpose of showing the nature of the working fluid we have constructed Table I. It will be seen from this that a mixture of 6·760

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enabling students to illustrate for themselves a course of lectures delivered by one of us on the Gas-engine. Hence we have taken the temperature of 410° C. as the exhaust temperature, instead of 300° C. given by our own measurements with the Siemens pyrometer. A correction of this temperature would perhaps lessen the number 1·57 W and increase 0·37 W, given in § 9.

cubic feet of air and coal-gas becomes, after complete combustion, 6·4977 cubic feet of carbonic acid, water-vapour, and nitrogen, reduced to the same pressure and temperature without condensation of the water-vapour. Now as there is always an excess of air, and as the mixture before combustion has added to it nearly six cubic feet of the products of previous combustions, we have something like 13·3 cubic feet before combustion becoming 13·0377 cubic feet after combustion, at equivalent pressures and temperatures. The contraction is only about 2 per cent. We therefore conclude that we may regard the fluid in a gas-engine as a fluid which, however it may receive heat, obeys approximately the characteristic law,

$$\frac{pv}{T} \text{ constant}$$

(where p is pressure, v volume, and T the absolute temperature), in so far as mechanical actions are concerned. That is, we may speak of it as a perfect gas, which receives heat from without, neglecting the fact that it is its own molecular energy which appears as heat. It is also approximately true that the ratio of the specific heats of the fluid is unchanged by combustion taking place.

In Table II. we give a similar comparison for Dowson gas :—

> 2·1325 cubic feet of combustible mixture become 1·9143 cubic feet ;

or, taking into account the clearance-space and its products of past combustions, we have, say,

> 4 cubic feet becoming 3·7818 cubic feet ;

or contracting by nearly $5\frac{1}{2}$ per cent. of its volume.

In Tables III. and IV. we calculate the specific heat of a mixture of 1 cubic foot of coal-gas, 5·76 cubic feet of air, and 4·5 cubic feet of products of a previous combustion, before and after combustion takes place. The Centigrade scale of temperature is employed.

In Tables V. and VI. similar calculations are made for the usual mixture of Dowson gas with air and products of previous combustion.

TABLE I.—Coal-Gas.

	Hydrogen, H_2.	Carbonic oxide, CO.	Marsh-gas, CH_4.	Olefiant gas, C_2H_4.	Tetrylene, C_4H_8.	Nitrogen, N.	Carbonic acid, CO_2.	Water-vapour, H_2O.	Total.
Cubic feet in one cubic foot of gas	0·4600	0·0750	0·3850	0·0253	0·0127	0·0050	0	0·0200	
Heat evolved per cubic foot of each	191·12	190·02	592·6	932	1702	0	0	0	
Heat evolved by given amount of each	87·92	14·25	234·1	23·58	21·61	0	0	0	381·46 or 530,230 foot-pounds.
Oxygen required by one cubic foot of each	0·5	0·5	2	3	6	0	0	0	
Product of combustion per cubic foot of each	1·0	1·0	3	4	8	0	0	0	
Oxygen required by given amount of each	0·2300	0·0375	0·790	0·0759	0·0762	0	0	0	1·2096 cub. ft. of oxygen per cub. [ft. of gas. or 5760 ,, ,, ,, air ,, ,, ,,
Volume of product of combustion	0·460	0·075	1·1850	0·1012	0·1016	0·005	0	0·020	1·9478+4·5499 of nitrogen, or 6·4977.

TABLE II.—Dowson Gas.

	Hydrogen, H_2.	Carbonic oxide, CO.	Marsh-gas, CH_4.	Olefiant gas, C_2H_4.	Tetrylene, C_4H_8.	Noncombustible.	Total.
Cubic feet in one cubic foot of gas	0·1873	0·2507	0·0031	0·0020	0·0011	0·5555	
Heat evolved per cubic foot of each	191·12	190·02	592·6	932·05	1702	0	
Heat evolved by given amount of each	35·79	47·63	1·837	1·864	1·872	0	88·99, or 123606·1 foot-pounds.
Oxygen required by given amount of each	0·0936	0·1254	0·0062	0·0060	0·0066	0	0·2378 cub. ft. of oxygen per cub. ft. of gas, or 1·1325 ,, ,, air
Volume of product of combustion	0·1873	0·2507	0·0093	0·0080	0·0088	0	·4641+·4898 of N in gas +·0657 of CO_2 in gas +·8947 of N in air introduced =1·9143.

TABLE III.—Coal-Gas before Combustion.

Constituent.	Amount in fluid.	Specific heat at constant pressure per unit volume.	Specific heat at constant volume per unit volume.		
	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Hydrogen	0·46	·2359	·99 ×·168	·1085	·4554×·168
Carbon monoxide	0·075	·237	1 ,,	·0178	·0750 ,,
Marsh-gas	0·3950	·3277	1·54 ,,	·1294	·6082 ,,
Olefiant gas	0·0380	·4106	2·03 ,,	·0156	·0771 ,,
Nitrogen	0·0050	·237	1 ,,	·0012	·0050 ,,
Water-vapour ...	0·0200	·2984	1·36 ,,	·0060	·0272 ,,
Air	5·76	·2374	1 ,,	1·3680	5·760 ,,
Products	4·5	·2581	1·124 ,,	1·1614	5·058 ,,
Total	11·253	......	......	2·8079	12·066 ×·168 or 2·027

Or $C_p = 0·2496$, $C_v = 0·1802$.   Ratio .... 1·385.

TABLE IV.—Coal-Gas after Combustion.

	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Water-vapour ...	1·3714	·2984	1·36 × ·168	·4092	1·865 ×·168
Carbon dioxide ...	0·5714	·3307	1·55 ,,	·1889	·8855 ,,
Nitrogen	4·5554	·2370	1 ,,	1·0790	4·5554 ,,
Total	......	......	......	1·6771	7·3059×·168 or 1·227

Or $C_p = 0·2581$, $C_v = 0·1889$.   Ratio ...... 1·367.

TABLE V.—Dowson Gas before Combustion.

	Cubic feet. q.	C_p.	C_v.	qC_p.	qC_v.
Hydrogen	·1873	·2359	·99 × ·168	·0442	·1854×·168
Carbon monoxide.	·2507	·237	1 ,,	·0594	·2507 ,,
Marsh-gas	·0031	·3277	1·54 ,,	·0010	·0048 ,,
Olefiant gas	·0031	·4106	2·03 ,,	·0013	·0063 ,,
Nitrogen	·4898	·237	1 ,,	·1161	·4898 ,,
Carbon dioxide ...	·0657	·3307	1·55 ,,	·0217	·1018 ,
Air	1·1325	·2374	1 ,,	·2689	1·1325 ,,
Products	2	·2594	1·1323 ,,	·5188	2·2646 ,,
Total	4·1322	......	......	1·0314	4·4359×·168
				·2496	1·0735×·168 or ·1803

Ratio .... 1·385.

TABLE VI.—Dowson Gas after Combustion.

	q.	C_p.	C_v.	qC_p.	qC_v.
Water-vapour ...	0·2019	·2934	1·36 × ·168	·0602	·2746 × ·168
Carbon dioxide ...	0·3279	·3307	1·55 ,,	·1084	·5083 ,,
Nitrogen	1·3845	·2370	1 ,,	·3281	1·3845 ,,
				·4967	2·1674 ,,
Total	1·9143	......	......	·2594	1·1323 × ·168 or ·1902
Ratio .... 1·3637.					

The specific heats here given are those of the constituents in the cold state. Seeing, however, that there is no great change due to combustion, we may for many practical purposes assume that the specific heats remain the same at all temperatures. We have less right when using Dowson gas than when using coal-gas to make our assumption, which is that the fluid in the gas-engine, from the beginning of its compression until it is allowed to escape, behaves like a perfect gas, receiving heat from an outside source.

4. *Study of the Shapes of the Compression and Expansion parts of the Diagram.*—The first problem which comes before us is the determination of the shape of the indicator diagram. For the sake of illustration we mean to investigate the series of diagrams shown in fig. 1, diagrams taken from a 6-horse power Otto engine at the Finsbury College, using coal-gas. It will be observed that, although the ignition parts of the various diagrams differ greatly, on account of differences *in the amounts of gas supplied*, the curves agree in their compression and expansion parts. It is known to us that the clearance-space is 0·4 of the whole space occupied by fluid when the piston is fully at the end of its stroke. If λ is the distance in feet passed through by the piston from the end of its stroke, the stroke being $1\frac{1}{3}$ foot, the clearance is 0·889 foot, and $\lambda + 0·889$, or l feet expresses the volume of the fluid at any instant. Measurements of l and p were made on the expansion-curves of the indicator-diagrams, and tabulated with $\log l$ and $\log p$.

We are making arrangements for measuring the clearance-space with accuracy. The above assumption is made from statements of the manufacturers, and may possibly be slightly in error. Such an error is of but small importance to us at present, as our object is to teach a method of study rather than to give results of the use of the method.

If we assume the law of the expansion-curve to be

$$pl^m \text{ constant,}$$

we have $\log p + m \log l = k$; so that when we plot $\log p$ and $\log l$ on squared paper as coordinates of points, these points ought to lie in a straight line if our assumption is correct. Fig. 2 (Pl. III.) shows how the points determined by the measured numbers lie; and it is obvious that they lie very nearly in a straight line. Taking the straight line which lies most evenly among them, we find that it is defined by

$$\log l = 0\cdot313, \quad \text{when } \log p = 1\cdot7,$$
$$\log l = 0\cdot0425, \text{ when } \log p = 2\cdot1.$$

Hence

$$1\cdot7 + 0\cdot313 \, m = k,$$
$$2\cdot1 + 0\cdot0425 \, m = k.$$

Hence

$$m = 1\cdot479 \text{ and } k = 2\cdot1629.$$

Now

$$\log 145\cdot5 = 2\cdot1629.$$

Hence the law of expansion is

$$pl^{1\cdot479} = 145\cdot5. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the same way we find that the law of the compression-curve is

$$pl^{1\cdot304} = 39\cdot36. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is obvious that the expansion-curve (1) is steeper than the adiabatic, if we assume that the ratio of specific heats of the fluid is $1\cdot37$, as the equation of the adiabatic curve is

$$pl^{1\cdot37} = \text{ constant.}$$

Again, the compression-curve (2) has less slope than the adiabatic.

5. *Influence of Vibrations of the Indicator-spring.*—We wish to point out that it is exceedingly necessary, in obtaining the law of expansion, to take many points in the curve, and, either by using the algebraic method or by the use of squared paper, to determine the most probable values of the constants. Engineers are constantly in the habit of determining these constants from measurements of the coordinates of two points only in the curve, forgetting that the position of either point may be much influenced by the vibrations of the spring of the indicator. The sinuous shape of the expansion-curve is

specially noticeable in the early part of the expansion-curves of gas-engine diagrams.

It is further to be remarked that the vibration of the indicator-spring is very visible in the expansion part, because we have every reason to believe that the expansion part ought to have no sinuosities ; but it is our belief that this vibration has its effect on the explosion part of the curve as well, and that it is of the utmost importance to find some means of eliminating the effects produced by these vibrations of the indicator-spring.

In our communication to the Journal of the Society of Telegraph Engineers, p. 391, vol. v. (1876), we showed how to eliminate such vibrations in any case where the effect to be measured followed a regular law of increase or diminution, as in the case of the expansion part of this indicator-diagram. We have not yet sufficient information to enable us to employ this method on the explosion part.

The rule which we arrived at is as follows :—Draw two curves, A and B, through the highest and lowest points of the wavy curve which represents the actual observations : draw ordinates : the points of bisection of the parts of the ordinates intercepted between A and B lie on the correct curve.

6. *Empirical Formula for the whole Diagram.*—Now, inasmuch as the compression and expansion parts of all the curves follow the same laws, it would seem to be important to obtain one general formula for all the diagrams with one or more variable parameters. We have found that when we produce the expansion-curve (using formula 1), as shown at B M (fig. 1), and when we divide the pressure Q R at any part of the stroke by the corresponding ordinate L R of the expansion-curve, doing this for many parts of the stroke, we get the ordinate of an interesting curve. We have done this for the four diagrams of fig. 1, and obtain the four curves A Q B D, A E C D, A F D, A G H of fig. 3. From a study of these curves, which are nearly formed of straight lines, it will be found that the ignition and expansion parts of any diagram satisfy approximately the law

$$p = 145 \cdot 5 \, l^{-1 \cdot 479} \left\{ \kappa' + n\lambda - \sqrt{(\kappa - n\lambda)^2 + s} \right\}. \quad . \quad . \quad (3)$$

The smaller the value of s the more nearly do the curves of fig. 3 approach straight lines. In our present case $\lambda = l - 0 \cdot 889$, $\kappa' = 0 \cdot 6343$, $\kappa = 0 \cdot 3637$; $s = 0 \cdot 0087$, and n has different values for the four diagrams. These constants are evidently easily calculated from any diagrams. For the curve shown as A B C D in fig. 1 (Pl. III.) the value of n is $2 \cdot 2876$. Using this value and calculating p for the following values of l, we have

TABLE VII.

λ.	l.	Observed. p.	Calculated. p.	Expansion-curve calculated. p.
0	·889	45	45	173
·061	·950	86	83	157
·111	1·000	108	108	146
·170	1·059	123	124	134
·211	1·100	126	125	126
·311	1·200	111	111	111
·511	1·400	88	88	89
·711	1·600	72	73	73
·911	1·800	60	61	61
1·111	2·000	52	52	52

The differences between the observed and calculated values of p are within the limits of errors of observation therefore. It may be that there is a discontinuity in the ignition-curve at $\lambda = ·061$ for a mixture of gas and air; but no discontinuity shows itself in the indicator-diagram in a sufficiently marked manner to be distinguished from vibrations due to the spring of the indicator.

As we have already stated, the recentness of the last explosion affects the temperature of the mixture of gas and air, and therefore the mass of the mixture. Hence we often find that the expansion parts of successive indicator-diagrams do not coincide. The law

$$p = \mathrm{M}l^{-1·479}\left\{\kappa' + n\lambda - \sqrt{(\kappa - n\lambda)^2 + s}\right\},$$

where κ', κ, and n are constants, satisfies all the diagrams.

n is a constant whose value depends on the point in the stroke at which the maximum pressure occurs; and this, for a given speed of engine, depends principally on the proportion of gas to air in the mixture;

M is a constant which depends on the recentness of the last explosion.

7. *Simple Formulæ for the Ignition and Expansion parts of the Diagram.*—The complete formula (3) assumes no want of continuity in proceeding from the ignition to the expansion part of the diagram. For the sake of ease in practical calculations we may, however, assume that the ignition- and expansion-curves are quite discontinuous, employing some method of indicating continuity when results are plotted on squared paper. In this case we assume that the lines of fig. 3 are

F 2

quite straight, so that

the ignition part of curve is $(a + b\lambda)\kappa l^{-m}$,   .   .   (4)

the expansion part of curve is κl^{-m}.   .   .   .   .   (5)

In our diagrams,

$$\kappa = 145 \cdot 5, \quad m = 1 \cdot 479;$$

Also $a = 0 \cdot 257.$

In curve A B C D, $b = 4 \cdot 372;$

„   A E D, $b = 1 \cdot 457;$

„   A F D, $b = 0 \cdot 782;$

„   A G H, $b = 0 \cdot 313.$

To use formula (4) in any given case.   Find by the method already given in § 4 the constants of equation (5) to the expansion part.   Assume that the ignition is complete when $\lambda = \lambda_1$.   Let the pressure at the beginning of the stroke be p_0; calculate the value of κl^{-m} when $\lambda = 0$, that is, when $l = $ clearance or l_0, say; then

$$p_0 \div \kappa l_0^{-m} \text{ is } a,$$

and

$$a + b\lambda_1 = 1;$$

so that

$$b = \frac{1 - a}{\lambda_1},$$

or

$$a = \frac{p_0}{\kappa} l_0^m \text{ and } b = \frac{1 - \frac{p_0}{\kappa} l_0^m}{\lambda_1}.$$

8. *The Rate at which the Fluid receives Heat as calculated from its Volume and Pressure.*—We shall now proceed to calculate the heat received by the fluid.   This we shall do as if, instead of there being combustion going on among the particles of the fluid, we had the fluid a perfect gas receiving heat from a great number of little furnaces, or pieces of hot wire immersed in the fluid.   Besides the heat here considered we have the heat radiated to the cold cylinder.

If A is the area of the piston in square inches, p the pressure of the fluid in pounds per square inch, and l the distance moved through by piston in feet, the work done by the fluid on the piston in an element of length dl is

$$A p \, dl \text{ foot-pounds.}$$

It is evident that if we represent the heat which is received by the fluid in the length dl by

$$A q \, dl \text{ foot-pounds,}$$

we may regard q as the rate (per foot-travel of the piston) at which heat is received by the fluid, just in the same sense as p the pressure is the rate at which work is done by the fluid ; and a comparison of q and p shows at once the comparison between the rates at which heat is being received and work is being done.

Now, since we consider the fluid to behave like a perfect gas, we know from thermodynamics that

$$q = \frac{1}{\gamma - 1}\left(\gamma p + l\frac{dp}{dl}\right), \quad \ldots \quad \ldots \quad (6)$$

where $\gamma = 1 \cdot 37$ (see §§ 3 and 4) ; and it is obvious that the relation of p to q is not altered in any way by altering the scale to which l or p is represented in the indicator-diagram.

We have taken three methods of drawing the curve whose ordinate is q. In the first method a list of the values of p was made out from careful measurements of the curve A B C D (fig. 1), for values of l, 0·889, 0·9, 0·911, 0·922, 0·933, 0·944, &c. The observed increment of p divided by the increment of l was taken to represent the value of $\frac{dp}{dl}$ for the mean value of l. In this laborious way q was obtained for many values of l, and the curve E F G H (fig. 4) represents our result. It is obvious that the rate at which the fluid receives heat is greatest at the very beginning of the stroke, falling off during the ignition period, much more rapidly at the end of the ignition period ; and in G H we see that the fluid is losing heat during what we call the expansion part of the stroke. In the same figure the actual indicator-diagram is shown in A B C D, the pressure being shown to the same scale as the ordinate of the heat-diagram.

The area between E F G H, the line Oλ, and any two ordinates, shows in foot-pounds the heat given to the fluid between the two positions, to the same scale as that to which the area of the indicator-diagram represents work done.

Another method which we have taken is this. To find q corresponding to a point S (fig. 5) on the indicator-curve. Draw a tangent S R to the indicator-curve, meeting the line O P in R. O P and O L are the lines O P and O L of fig. 1. Draw from R a line R Q parallel to O L, meeting the ordinate from S in the point Q. Then the distance S Q, or rather TS−TQ, represents

$$l\frac{dp}{dl}.$$

Measuring S Q, therefore, paying attention to the fact that it

may be negative or positive, adding to it $\dot{\gamma}$ times S T and dividing by $\gamma-1$, we obtain the ordinate q of the heat-curve.

Another method is to calculate q as given in (6), by actual differentiation of p as given in (3). We have employed this method, and believe that our result, in which the early part of the curve E F (fig. 4) is less steep than there shown, is probably more nearly true than what is given in fig. 4. We do not put our result forward at present because there may be a discontinuity in the explosion part of the curve, as Table VII. shows that at $\lambda=\cdot061$ the empirical formula does not give the observed pressure; and until we know how to eliminate vibrational effects of the indicator-spring, we have preferred only to publish the curve E F G H which has been obtained from the actual diagram, the expansion part only having been corrected for vibrations. As we know that the expansion part follows a law

$$p=\kappa l^{-m},$$

it is obvious that

$$q=\frac{\gamma-m}{\gamma-1}p,$$

being proportional to the pressure. Now, comparing this result with the part G H (fig. 4), we see that G H is not quite correct, although determined from most careful measurements of the indicator-diagram. We see here an illustration of the great importance of obtaining a formula such as that given in (3) for the shape of the indicator-diagram.

9. *Total Heat and Work of One Cycle.*—The integral of $q \cdot dl$ multiplied by the area A of the piston in square inches gives the total heat received by the fluid during any part of the stroke, and is evidently

$$A\int_{l_1}^{l_2} q \cdot dl = \frac{A}{\gamma-1}(p_2 l_2 - p_1 l_1) + A\int_{l_1}^{l_2} p \cdot dl.$$

Taking from the diagram

$$p_1=44\cdot5, \quad l_1= \cdot889,$$
$$p_2=49\cdot0, \quad l_2=2\cdot089,$$

so that $l_2-l_1=1\cdot2$ foot (l_2 corresponds to the part of the stroke at which the exhaust-valve opens), it is evident that

$$\int_{l_1}^{l_2} q \cdot dl = 169\cdot5 + \int_{l_1}^{l_2} p \cdot dl. \quad . \quad . \quad . \quad (7)$$

Or if q_m is the mean value of q during this portion of the

stroke, and if p_m is the mean value of p, then

$$1\cdot2\ q_m = 169\cdot5 + 1\cdot2\ p_m,$$

or

$$q_m = 141\cdot25 + p_m.$$

We find from the diagram that $p_m = 94\cdot5$, so that $q_m = 235\cdot75$.
   Now $1\cdot2\ \mathrm{A}q_m$ is H, the total heat given to the fluid to alter
         its volume and pressure until the exhaust-valve opens;
   $1\cdot333\ \mathrm{A} \times 61\cdot52$ is the indicated work W of the cycle, as
         calculated from the total indicator-diagram, including
         the dismission and suction parts not shown in fig. 1.

Hence $\qquad \mathrm{H} = \dfrac{1\cdot2 \times 235\cdot75}{1\cdot333 \times 61\cdot52}\,\mathrm{W}$, or $3\cdot45\ \mathrm{W}$.

   As we know that combustion, about the period of opening
of the exhaust-valve, is just sufficient to supply the loss by
radiation to the cylinder without having much effect on the
volume and pressure of the fluid, we can assume that any
combustion after that time produces heat which is radiated to
the cylinder. We are told that there is no combustion in the
exhaust. For the small amount of combustion after the
exhaust-valve opens we do not see our way at present to the
basis of any but the very roughest assumption, and we think
that attention ought to be paid to this matter in future inves-
tigations. What complicates the question is the fact that the
mass of the fluid which radiates heat to the cylinder rapidly
gets less after the exhaust-valve opens. To obtain a first
approximation, we may assume that the heat of combustion
after the exhaust-valve opens is equal to the work done in the
forward stroke after that time—that is, $0\cdot14$ W.
   The heat retained by the fluid is $141\cdot25 \times \mathrm{A} \times 1\cdot2$, or $1\cdot94\,\mathrm{W}$.
   The gases in the exhaust-pipe close to the cylinder are
known to have a temperature not much greater than $400°$ C.
Hitherto it has been customary to calculate the amount of
heat carried off by the gases through the exhaust-pipe from
the heat-capacity multiplied by the difference of temperature
from that of the atmosphere. It must be remembered, how-
ever, that the total heat of combustion of coal-gas contains the
latent heat of the steam produced, and that the exhaust gases
carry off this heat. Hence the amount of about $0\cdot95$ W, de-
ducible from the experiments of Messrs. Brooks and Steward,
must be increased by two thirds of itself, giving $1\cdot57$ W as the
energy carried off by the gases in the exhaust-pipe.
   Hence $(1\cdot94 - 1\cdot57)$ W, or $0\cdot37$ W, is the amount of energy
which is lost by the fluid from the opening of the exhaust-
valve until the fluid is passing along the exhaust-pipe outside

the cylinder.   This is largely expended in heating the cylinder itself, in friction at bends in the exhaust-valve, &c.; so that it disappears as radiated heat, and as heat given to the water-jacket during the remaining parts of the cycle.   Now we may safely take it that the expenditure of gas is about 22 cubic feet per hour per indicated horse-power; so that, using the heat of combustion calculated in Table I., the total energy of combustion of the gas used is 5·91 W; and we are now in a position to make the following table.   Of the 5·91 W, the total energy of combustion of a charge, we have:—

- 1·38 W. Work of forward working-stroke till exhaust-valve opens.
- 0·14 W. Work of forward working-stroke after exhaust-valve opens.
- 2·31 W. Heat given to the cylinder during forward work-ing stroke by radiation before exhaust-valve opens*.
- 0·14 W. Heat of combustion after exhaust-valve opens and which is radiated to the cylinder.
- 1·57 W. Heat carried off by gases in exhaust-pipe.
- 0·37 W. Given to the cylinder as heat after the exhaust-valve opens, partly by friction at the exhaust-valve, partly during the succeeding three fourths or non-working parts of the cycle.

It is found by experiment that the water from the water-jacket carries off somewhat more than 50 per cent. of the total heat of combustion, or 2·96 W; but it is almost impossible to make this measurement accurately for one cycle.   It is some-times as much as 62 per cent. and sometimes as little as 35 per cent.   We have not employed such a measurement here, partly for this reason, and partly on account of the rate of loss during three fourths of the cycle being indeterminate.   Again, the cylinder loses heat by radiation as well as by the water-jacket; so that, even if we could assume that such a number as

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* It may be well to state here that we do not know with certainty the amount of gas used per indicated horse-power when the particular diagram which we are discussing was being taken, nor are we quite sure that Mr. Clerk is right in saying that the exhaust-gases show complete combustion when the engine is working to its full power.   Our arrangements for determining this latter point are now nearly complete. We consider that there was no possibility of the expenditure having been less than 20 cubic feet per hour per indicated horse-power when our dia-gram was taken; and if we take 24 as a higher limit, and assume with Mr. Clerk that combustion is complete in the exhaust-pipe, we find the amount of heat given to the cylinder during the forward-working stroke by radiation before the exhaust-valve opens could not have been less than 1·77 W, the higher limit giving 2·85 W.

50 per cent. is correct, we are still not in a position to state the total loss of heat from the cylinder.

It is to be remembered that W is the indicated work. The useful work of a gas-engine, given out by the crank-shaft, is about $0 \cdot 8\ W$, there being an expenditure of $0 \cdot 2\ W$ in overcoming the mechanical friction of the engine.

10. It is unnecessary to put before the Society the curves obtained by us by employing (6) on the discontinuous expressions of § 7 for the indicator-diagrams.

11. *Rate of Loss of Heat by the Fluid during Compression.*— For the compression part of the diagrams,

$$\gamma = 1 \cdot 385,$$

and

$$p = 39 \cdot 36\ l^{1 \cdot 304}.$$

Rate at which heat is received by fluid is $-q$, if

$$q = \frac{1}{\gamma - 1}\left(\gamma p + l\frac{dp}{dl}\right);$$

and by § 8,

$$-q = \frac{36 \cdot 36\ l^{1 \cdot 304}(m - \gamma)}{\gamma - 1}$$

$$-q = l^{1 \cdot 304}\ 39 \cdot 36 \times \frac{m - \gamma}{\gamma - 1},$$

$$m - \gamma = - \cdot 081,$$

$$\gamma - 1 = \cdot 385.$$

Therefore the rate at which heat is received by fluid is

$$-0 \cdot 2104\ p,$$

being proportional to the pressure, and is negative—that is, the fluid is radiating heat to the cylinder.

12. *Rate at which Fluid radiates Heat to cold Cylinder.*— It was found by the pyrometric measurements of Messrs. Brooks and Steward that the temperature of the products of combustion in the clearance-space, if there has been a recent explosion, is about 410° C.; and for the purpose of determining the temperature of the fluid before compression, they take 1·4 volume of coal-gas and 9·25 of air at 22° C. with 7·94 volumes of products of past combustions at 410° C., from which, assuming that the specific heats of the constituents do not alter with temperature, they find that the temperature of the mixture before compression is 120° C. This is sufficiently correct for our present purpose, and if we take it as the temperature when $l = 2 \cdot 222$, $p_0 = 14 \cdot 7$, we can find the temperature corresponding with any point of any of the indicator-diagrams.

We have made the calculations for various points on curve
A B C D (fig. 1), knowing that $pl \div T$ is constant (see § 3).

<div align="center">TABLE VIII.</div>

l.	p.	Absolute temperature. T.	Temperature of fluid. $t°$ C.	$t°$ —60° C.	Ordinate of semicircle.	Ratio.
·889	44·5	476	203	143	0	∞
·949	86	982	709	649	28	23·18
·989	105	1244	974	914	35·5	25·74
1·089	126	1644	1371	1311	48	27·33
1·389	90	1496	1223	1163	65	17·89
1·689	66	1344	1071	1011	66	15·32
2·089	49	1231	958	898	40	22·45

From some diagrams examined by us we find that the fluid
may have as high a temperature as 1900° C.

The temperature of the water leaving the water-jacket was
about 60° C.; and we may for our purposes assume that the
rate at which the fluid loses heat to the cylinder is proportional
to the excess of its temperature above 60° C., so that $t-60°$
represents, to some scale, the fluid's loss of heat to the
cylinder per second. This rate of loss is shown on the curve
A B (fig. 6).

Now if H is the quantity of heat which has been given by
the fluid to the cylinder-jacket at the time τ, then $\dfrac{dH}{d\tau}$ is
represented by the ordinate of the curve A B.   But

$$\frac{dH}{d\lambda} = \frac{dH}{d\tau}\frac{d\tau}{d\lambda} \text{ or } \frac{dH}{d\tau} \div \frac{d\lambda}{d\tau};$$

and as the piston-motion is very nearly

$$\lambda = r(1 - \cos a\tau),$$
$$\frac{d\lambda}{d\tau} = ra \sin a\tau ;$$

that is, $\dfrac{d\lambda}{d\tau}$ is proportional to the ordinate of a semicircle C E F.

Describing the semicircle C E F with a diameter equal to the
length of the stroke, and dividing the ordinates of A B by
those of C E F, we obtain the curve G H I, whose ordinate at
any point represents the rate of the fluid's loss of heat to the
cylinder per foot of piston-motion ; so that the whole area

C G H I F represents the total loss of heat to the cold cylinder during the stroke. We are in a position to speak of the loss of heat from $\lambda=0$ to $\lambda=1\cdot2$ (see § 9).

This loss must be represented on the diagram to the same scale as the indicator-diagram represents work done, and it is expended in the part of the working stroke from $\lambda=0$ to $\lambda=1\cdot2$. Hence if k is the mean ordinate of such a diagram,

$$k=2\cdot31 \times 61\cdot52 \times 1\cdot330 \div 1\cdot2 = 158.$$

Now the mean ordinate of the curve G H I (fig. 6) from $\lambda=0$ to $\lambda=1\cdot2$ being taken and found different from 158, all the ordinates of G H I (fig. 6) have been diminished in the proportion of 158 to the mean ordinate of G H I (fig. 6) to get the diagram X L Y of fig. 4. This diagram X L Y represents the rate of loss of heat by conduction and convection from the fluid to the cylinder during the working stroke until the exhaust-valve opens.

13. *Rate at which Combustion goes on during the Stroke.*— The curve E F G H represents the rate at which heat is actually gained by the fluid, and X L Y shows the rate at which heat is wasted to the cylinder ; so that the curve I J K Y shows at every point the rate at which heat is being generated in the fluid by combustion. It is obvious, then, that combustion is not complete at the end of the explosion part of the curve, although, as Mr. Clerk's experiments prove, the mixture of air and gas is in the proper proportions for explosion immediately behind the piston at all periods of the compression-stroke. The diagram I J K Y is specially valuable, as showing the effect of dissociation of the products of combustion at such temperatures as obtain in the gas-engine, and are shown in Table VIII.

Postscript, *added June 10th.*—We have assumed in the paper that the rate of loss of heat by radiation and convection is proportional to the difference between the mean temperature of the fluid and the temperature of the cylinder. When we have more information concerning the distribution of heat in the fluid, and the way in which a heated fluid loses its heat to a cold enclosing vessel, a more accurate assumption may be made; and it is easy to see what alteration this will introduce in our method of obtaining the curve X L Y (fig. 4).

It is known from the experiments of MM. Dulong and Petit that the rate of cooling by radiation and convection of a solid body increases more rapidly than the difference of temperature, and that it is greater at greater pressures of the gaseous medium between the hot body and the surrounding cold vessel.

We are now engaged in an investigation involving much higher differences of temperature than those of MM. Dulong and Petit; and in so far as we have obtained results for temperatures extending from about 800° C. to 1300° C., we have confirmed the conclusions of these gentlemen. Thus the loss of heat per second at 776° C. being 97·2, the loss at 1292° C. is 253·2.

Our method of experimenting is, we believe, new. The heated body is a spiral of platinum, whose change of electric resistance when there is change of temperature is known. It is surrounded by a vessel, blackened inside and maintained at constant temperature. An electric current is made to pass through the platinum spiral, maintaining it at any required temperature. An ammeter and voltmeter enable the current A and the difference of potentials V between the ends of the platinum spiral to be measured. Then VA is the rate at which heat is being radiated from the platinum, and V / A is the electric resistance of the platinum, from which its temperature is known. We intend to investigate the influence of high pressures of air and other gases.

We are somewhat doubtful as to the weight which we ought to give to the results obtainable from these experiments on the loss of heat by solid bodies, since in our gas-engine investigations, we deal with a mixture of hot gases; and in adopting the law of simple proportionality to difference of temperature, we have been influenced by the fact that rate of loss of heat by the fluid in the compression-stroke increases much more slowly than is indicated in Dulong and Petit's law, although the pressure of the fluid is increasing as well as its temperature. The result given in § 11 is to the effect that during compression the rate of loss of heat by the fluid is nearly proportional to the $\frac{13}{23}$ power of the absolute temperature of the fluid, or to

$$(\theta + 333)^{\frac{13}{23}},$$

if θ is the difference of temperature from 60° C., the temperature taken as that of the cold cylinder. If q is this rate of loss, it is obvious that $\frac{dq}{d\theta}$ diminishes as θ increases. It will be observed that the probability of the piston's having a high temperature causes this result to be even more curious than it might otherwise appear to be.

VII. *Notices respecting New Books.*

Die Magneto-elektrischen und dynamoelektrischen Maschinen, by
GUSTAV GLASER-DE CEW; and *Die Elektrische Kraftübertragung,
und ihre Anwendung in der Praxis*, by EDUARD JAPING; being
Vol. I. and Vol. II. of *Hartleben's 'Elektrotechnische Bibliothek.'*
Vienna, 1883.

THESE little volumes are the first two of a series on electro-
technical subjects announced by the same publisher. Their
appearance is probably due to the recent rush on electric inventions.
The first of these volumes, dealing not only with dynamo-electric
machines, but also with the so-called secondary batteries and with
various kinds of measuring-instruments, is decidedly of the semi-
popular order; though the formulæ and data which it comprises will
doubtless be of advantage to engineers and electricians. The first
hundred pages are purely descriptive of the different kinds of
machines. Switches and secondary batteries take up another forty.
Pages 143 to 172 are occupied in discussing the chief mathematical
laws of the dynamo, including the rules for efficiency given by Sir
W. Thomson, and the arguments of Frölich on the equations for
the current. In the equations there are sundry typographical
errors. After this come short chapters on the construction of the
separate parts; on the application to electric lighting and other
industrial purposes; and, lastly, on electrical measuring-instru-
ments.

The second volume possesses both the merits and the defects of
the first. Both are handy, well printed, clearly written; the
second perhaps better than the first. It begins with an argument
on the conservation of energy, and then describes in detail a large
number of forms of electric motor. A considerable section of the
book is given up to a description of the different kinds of cables
and conductors; and another to the applications made by Deprez
of the characteristic curves of Hopkinson and Deprez. The author
appears to doubt whether a dynamo machine can be constructed
to give a constant potential at the terminals automatically. Secon-
dary batteries come in again as applied to systems of electric
distribution; and the work closes with a number of examples of the
actual employment of electric power in Siemens's electric tramway,
Hopkinson's electric lift, the recent electric launches, and other
instances.

*An Elementary Treatise on the Planetary Theory, with a collection of
Problems. By the late* C. H. H. CHEYNE, *M.A.* London: Mac-
millan and Co. 1883. (Pp. xiv + 165.)

THE author of this work died at Torquay, January 1, 1877, and a
new edition (the third) is now, at his father's request, brought out
under the competent editorship of the Rev. A. Freeman, late
deputy Plumian Professor at Cambridge. Such being the case,
there is no need of a further introduction for a work which has

already made its mark. The editor, besides having carefully revised the text, has added a few brief notes and some dozen problems extracted from recent Tripos and Smith's Prize papers. We should prefer a treatise of this kind in a somewhat larger size, as the formulæ are long and make the pages look crowded: on the other hand, the present form is handier for use.

VIII. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETISM OF ORGANIC BODIES.
BY S. WLEÜGEL AND S. HENRICHSEN.

THE authors have examined the magnetism of some compounds of the alcohol radicals C_nH_{2n+1}. The bodies in question, which were partly prepared by the authors themselves and partly obtained from M. Kahlbaum, were all carefully purified before being used. For the measurements, they were placed in a small glass vessel. This was of a somewhat long horizontal shape, and had a bifilar suspension, so that it oscillated between the pointed half-armatures of a large horseshoe electromagnet. The current was that of 16–18 Bunsen's elements. The magnetism excited in the bodies was measured by a torsion method with a mirror reading like that previously used by G. Wiedemann. The results are collated in the following table; m is here the specific magnetism, that of water being -100, μ is the molecular magnetism, and q the molecular weight. The negative prefix indicates diamagnetism. The magnetism of the displaced air was taken into account.

The numbers here given are only provisionally to be considered as correct, as the authors wish once more to test the purity of the substances used. They are, however, sufficiently trustworthy to justify several interesting conclusions.

	m.	*μ.*	*q.*
Methylic alcohol	−94·40	−3021	32
„ iodide	58·01	8238	142
„ sulphate	102·34	6345	62
„ acetate	80·90	5987	74
Ethylic alcohol....................	101·09	4759	46
„ iodide	61·96	9665	156
„ bromide	68·90	7511	109
„ sulphide	105·48	9493	90
Propylic alcohol	107·51	6451	60
Isopropylic alcohol	107·51	6451	60
Propylic iodide	66·65	11331	170
„ bromide	74·48	9161	123
„ chloride	100·08	7857	78·5
„ sulphide	107·84	12729	118
Isobutyric alcohol	109·80	8125	74
„ acetate.................	96·07	11167	116
Water	100	1800	18

1. In considering the column μ it will be seen that the introduction of CH_2 into the compound produces an increase in the molecular magnetism which is almost constant, and the mean value of which is -1640.

2. If the chemical formula of a body is at the same time to indicate its specific magnetism, we can establish the following equations:—

$$15\,CH_3 + 17\,HO = 32\,CH_3\,HO,$$

$$15\,CH_3 + 127\,I \quad = 142\,CH_3\,I,$$

$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot$$

$$29\,C_2\,H_5 + 17\,HO = 46\,C_2\,H_5\,HO,$$

$$58\,C_2\,H_5 + 32\,S \quad = 90\,(C_2\,H_5)_2\,S,\ \&c.$$
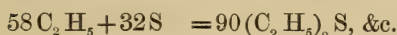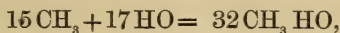
The molecular magnetism of the entire body is thus equal to the sum of the partial magnetisms of the alcohol radical and of the other parts of the compound.

3. In these compounds, HO, I, Br, and S have the same specific magnetism, the mean value of which is $-44\cdot3$.

4. On the other hand, it is strange that Cl has a different specific magnetism of about -61; it must, however, be remarked that only a single chloride was examined. It is nevertheless interesting that the two acetates give for the radical of acetic acid nearly the same magnetism as that found for Cl—that is, -63 in the mean. There is possibly a group of radicals with the specific magnetism about -62.

5. Propylic alcohol and isopropylic alcohol show exactly the same value; and isobutyric alcohol gives the value which is calculated for butylic alcohol from the law (1). So far as examined, the alcohol radicals possess the same magnetism in their isomers.

6. The magnetism of the alcohol radicals is made up of the atomic magnetisms of the C and H, so that, as in (1), the following equations may be made:—

$$15\,CH_3 = 12\,C + 3\,H,$$

$$29\,C_2\,H_5 = 24\,C + 5\,H,\ \&c.$$
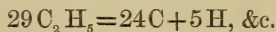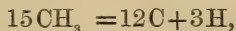
If we calculate from this C and H, we get for H the rather large value $-780\cdot5$, while C is only $-5\cdot6$. The latter number is numerically so small in comparison with -780, that no importance can be assigned to it. The equations are just as well satisfied by $C = 0$ and $H = 807\cdot6$.

The investigations are being continued, and the influence of temperature will especially be taken into account.—*From an Abstract, communicated by the Authors to* Wiedemann's *Annalen*, No. 5, 1884.

ON THE MANNER IN WHICH THE CURRENT OF AN INDUCTION
FRICTIONAL MACHINE IS AFFECTED BY THE MOISTURE. BY
R. KRÜGER.

The results of this investigation may be summarized as follows:—

1. The connexion between the strength of the current of an induction machine and the moisture may be expressed by the formula

$$i = i_0 - \alpha\rho^2 = i_0 \left(1 - \frac{\rho^2}{\rho_0^{\,2}} \right);$$

in which i is that strength of current which would be obtained if there were no moisture at all, and ρ_0 is that degree of moisture at which the machine would not work. This formula holds for any degree of relative moisture with perfect accuracy.

2. The constant $\rho_0 = \sqrt{\dfrac{i_0}{\alpha}}$ is greater as the velocity of rotation increases; that is, when the machine is rotated with greater velocity, its current first disappears at higher degrees of moisture than when the rotation is less rapid.

3. The quantity of electricity given by one turn of the plate when there is no moisture is essentially independent of the velocity of rotation; and the quantity of electricity which in this case passes through the section of the conducting wire amounts to $458,33 \cdot 80^5$ electrostatic units.

Some observations intended to ascertain how far the current depends on the distance of the points from the movable plate, and, on the other hand, on the distance of the plates from each other, showed a decrease of strength with greater distance; but it was not possible to establish a definite law.—Wiedemann's *Annalen*, No. 6, 1884.

BOYLE'S LAW. A LECTURE EXPERIMENT.
BY J. L. ANDREAE.

In a glass tube, about a metre long and from $1\frac{1}{2}$ to 2 millim. internal diameter, closed at one end and open below, is introduced a thread of mercury about 250 millim. in length. This encloses a certain volume of air, which is about 40 cub. centim.

The tube is supported on a stand, which has a scale on white paper divided in centimetres, and can be placed on the table with either end vertical. If H is the height of the barometer in millimetres, the pressure of the enclosed air is P = H − 250. If the tube is inverted, the pressure is P′ = H + 250. If H = 750, P = 500 and P′ = 1000, so that the volume is reduced from 40 to 20.

This simple apparatus has the advantage that it is always ready for use, and hence does not need to have the mercury poured in as in the usual form.—Wiedemann's *Annalen*, No. 6, 1884.

IX. *On a new Apparatus for Colour-Combinations. By* H. H. HOFFERT, *B.Sc., A.R.S.M., Assistant in the Physical Laboratory, South Kensington*[*].

VARIOUS arrangements for the mixture of colours have already been devised by Maxwell, Rayleigh, Helmholtz, and others, by means of which the laws of colour-combinations have, in their main features, been firmly established.

Wishing to observe for myself the principal phenomena connected with this subject, I have repeated, during the past winter, many of the experiments thus described, both with the colour-top and with overlapping spectra. Being desirous of obtaining some convenient arrangement whereby any two or three colours of the spectrum could be combined in any required proportion, and compared with the colours either of natural objects or of other spectral combinations, I tried various experiments, using the method first adopted by Maxwell, of observing, by means of a slit-eyepiece, the spectra produced by light proceeding from illuminated slits, and passing through a train of glass prisms; this method being equivalent to looking through a hole in a screen on to which are cast two or three superposed spectra, so that the colour perceived is that due to the mixture of those parts of the several spectra which fall on the hole.

In these experiments I have been assisted by my colleague

Mr. Mitchell, to whom I am also indebted for several valuable suggestions.

We first tried a modified form of Maxwell's colour-box, using eventually six equilateral glass prisms, arranged in two sets of three symmetrically with respect to the eyepiece; so that if the latter be made a source of light, the rays are bent through about 150°, and being then received on to a lens, are focused on to planes situated on either side of the eyepiece, this arrangement being found very convenient for manipulation.

Movable slits of fixed width, sliding in a frame with bellows-screens of opaque silk between, were used as sources of light, lamps being placed outside them. The intensity of the light was regulated by means of Nicol prisms, one being attached to each slit, so as to be capable of rotation, while an analyzing Nicol was fixed in the eyepiece. The intensity could thus be readily altered for each slit separately.

This arrangement was found to answer fairly well, but its necessarily large dimensions were a great inconvenience. A very long spectrum was needed, as the slits could not be brought very close on account of the size of the Nicol prisms; hence also there was great loss of light.

Movable slits, whether of fixed or adjustable width, are very troublesome to manipulate, and do not admit of very rapid and easy adjustment; they were therefore abandoned altogether, and in their place the light from small lengths of platinum wire, heated to incandescence by an electric current, was employed. Preliminary trials having proved satisfactory, the apparatus was constructed which I now bring before your notice.

The prisms, lenses, and sources of light are enclosed in a flat box of irregular hexagonal shape, at the smaller end of which the six prisms (P, Pl. V.) are placed. These are arranged, as already described, in two sets of three, each prism being set to minimum deviation. The first prisms have their refracting-edges in contact; and by means of a screen (S), in which is a small rectangular aperture, small equal strips of the adjacent faces of these prisms are visible from the eyepiece (E), which is a small brass tube with a narrow slit, about $\frac{1}{16}$ inch wide.

Supposing light to come from the eyepiece, the prisms would deflect it through about 150°; it would then fall on to two lenses (L), of about 10 inches focal length, which focus the spectra on to the two sides of the box immediately to the right and left of the eyepiece. Here are placed the incandescent wires (W); so that, conversely, if these be the sources of light, the rays follow an inverse course, and the correspond-

ing half of the aperture in the screen is seen illuminated with a colour which will depend on the position of the incandescent wire, and which will be pure and uniform if the wire be not too thick, the slit in the eyepiece too wide, or the strip of the prism exposed too large. The colours are found in practice to be perfectly uniform.

The prisms and lenses are supported at the level of the incandescent wires, on a horizontal floor (G), which divides the box two inches from the top into two compartments, and which is cut away so as to leave a space for the tops of the frames carrying the wires to enter the upper compartment. These frames (W), which are six in number, three on each side, consist of brass wires held on small ebonite blocks (I), which slide along a steel rod (H) supported on a ledge inside the box. The frames can be moved along the length of the spectrum from outside by means of openings (A) cut in the sides of the box, into which the hands can be introduced. These openings are below the level of the horizontal floor, so that the upper compartment, which is everywhere blackened inside, is quite impervious to external light, unless the lids in the cover of the box, to be presently described, are opened.

The frames are connected by flexible wires to a series of resistances arranged in the lower compartment of the box; and by means of six dials (R), on the sides of the box, each of the six circuits can be altered in resistance at will, so that the incandescent wires can be rapidly adjusted, whether in position or in intensity, by the observer without his having to remove his eye from the eyepiece. Six pairs of binding-screws (T) at the back of the box connect the six circuits with a Grove battery. By this means, when the current is passing, the aperture in the screen is seen divided into two coloured strips in close juxtaposition ; one colour being that due to the wires and prisms on the right hand, the other to those on the left. The colours can thus be readily compared and adjusted to exact identity.

It remains to describe the means by which external colours can be introduced for comparison with those produced by the prisms.

The cover of the box contains three small hinged lids. Two of these (C) are over the luminous wires, and serve to adjust or replace the wires in case of accidental fusion. The third lid (D) opens over the space just in front of the screen. Here is placed a small strip of microscope cover-glass (M), inclined at about 60° to the horizontal, and so arranged that, as seen from the eyepiece, it exactly covers that portion of the aperture in the screen which is illuminated by the light from the

left-hand train of prisms, this light being thus seen through the glass slightly diminished in intensity. On the underside of the lid is a small silvered mirror (N); and by raising the lid to the proper height, the colour of any object laid on the top of the box is seen by double reflection in the eyepiece, exactly coinciding with the left half of the aperture in the screen. This colour may be either combined with that from the left-hand train of prisms, or compared with that from the right-hand train. For white light I use the light from a window, which may be reduced in intensity to any desired amount by passing it through one or more pieces of roughened glass, held in a frame placed on the top of the box. Coloured glasses, or cells of coloured fluids, can similarly be placed in the frame, so that almost every possible combination or comparison of colours may be made. Another frame, which may be placed inside the box between the screen and the eyepiece, serves to show the action of different absorbing media on colours identical in appearance but of different composition.

The colours produced are uniform, very constant, and fairly bright. Those from the blue and violet parts of the spectrum are necessarily more deficient in luminosity. This is partially compensated by using in the less luminous parts of the spectrum ribbons of platinum, produced by rolling out the wires, with their flat surfaces turned towards the lenses. This is equivalent to increasing the width of the slit in ordinary arrangements. Should the wires become fused through incautiously using too strong a current, they can be very readily replaced by means of the screws (K).

For the current, three Grove's cells are needed for each of the ribbons and two for each of the wires. But since the frames carrying the wires can be brought together till the wires are nearly in contact, and since the wires themselves offer extremely narrow luminous surfaces, a very long spectrum is not needed ; and by using more powerful lenses and bringing the sliding frames closer to them, a greater intensity of light would result; while the size of the box might thus be reduced to one half or even less of its present amount, the eyepiece being kept at a sufficient distance by the use of a longer tube, which might be made removable. One Grove cell would then suffice for each wire, or at most two when experimenting on the violet rays.

Instead of the step-by-step dial-resistances, some arrangement giving, like the rheostat, a gradual adjustment of the intensity would be perhaps preferable.

Scales can be attached in front of the sliding frames to

show the exact position in the spectrum of each of the luminous wires.

I trust that the ease and rapidity with which the adjustments in this apparatus can be made will cause it to be found useful in those many cases in which it is impossible or inconvenient to make use of the more powerful effect of direct sunlight.

X. *On the Electric Discharge in Gases.*
By EILHARD WIEDEMANN.

[Concluded from p. 54.]

6. *ON the Nature of the Kathode-rays.*—I showed, in my first paper on the Electric Discharge, that the kathode-rays cannot take any important part in the formation of the current and in the transport of the electricity. The strength of the current in a circuit in which a discharge-tube is included remained sensibly the same, whether the kathode-rays were allowed to radiate freely, or whether they were received upon a mica-screen. Recent experiments carried out by other methods by Hertz * lead to exactly the same result.

What conception, then, are we to form of the kathode-rays?

In the memoir referred to above, I have endeavoured to show that the view held by Crookes, Puluj, and others, according to which the kathode-rays consist of particles separated from the electrode and projected from it, cannot be sustained. Other reasons are given by Hertz and Goldstein†. Notwithstanding Herr Puluj, in later publications, without making any experiment to set aside our objections, and sometimes without even referring to them, insists upon his old views. The carrying of particles of the electrode along the kathode-rays is a secondary phenomenon, which has just as little to do with propagation of the motion which corresponds to it as the flight of a cannon-ball has to do with the radiation of the sound produced by the explosion. I

* Wied. *Ann.* xix. p. 782 (1883).

† Wied. *Ann.* xii. p. 263 (1881). In a reference in the *Fortschritte der Physik*, 1880, to my paper published in Wied. *Ann.* x. p. 802, Herr Goldstein asserts that I had incorrectly deduced arguments against motion in the kathode-rays from the experiments of Wheatstone and Von Zahr, and makes objection to them. But an attentive reading of the passage shows that I am considering only motion in the ordinary current, as is seen for example from the remark on p. 246:—"These considerations, which I had already used, Wied. *Ann.* ix. p. 160, to show that the transport of particles takes place *in the direction of the current*, Herr Goldstein has also repeatedly made use of in describing the processes which take place at the *negative* electrode."

believe we may explain all the peculiarities of the kathode-rays, in accordance with the views already expressed, by assuming that the kathode-rays represent light rays of very small oscillation-period *.

(1) From experiments by E. Goldstein†, which have been confirmed partly by myself‡, partly by Spottiswoode and Moulton §, it may be shown that the motions in the kathode-rays must certainly be supposed to be orientated in a certain way to the rays themselves. The experiments showed that the kathode-rays can traverse the positive light without hindrance if their motion of direction coincides with that of the positive light, and, further, that if a point of the wall be connected with the ground, and thus a kathode be produced at that point, shadows of the positive stratifications are thrown by the rays issuing from the wall. In this arrangement of the experiment the kathode-rays traverse the positive column of light at right angles. The experiments first mentioned show that we cannot, with Spottiswoode and Moulton, explain the phenomenon by supposing that larger quantities of matter are accumulated in the stratifications than in the dark spaces between them. For when the kathode-rays traverse the stratifications longitudinally, they must pass through larger quantities of matter than when this takes place transversely.

Since, then, in the second case we have a mutual disturbance and not in the first, we must conclude that the motions of the kathode-rays and of the positive discharge are opposite in direction. Since further disturbances occur, especially in motions which take place parallel to each other, the motion in the kathode-rays must be at right angles to that in the positive light. We may imagine the motion in the positive light as produced by a dielectric polarization which issues from the positive electrode, and which is then followed by a current of positive electricity‖. This motion is certainly longitudinal; the

* That the kathode-rays consist of waves in the æther, I have endeavoured to show in Wied. *Ann.* ix. p. 100, and Wied. *Ann.* x. p. 251. Messrs. Goldstein and Hertz have signified their adherence to this view.

In a recently published paper Herr Goldstein asserts that he was the first who considered the electric discharge as a motion of æther. This is not quite correct, as already in the year 1797 Gren had the same view for the electric light in the vacuum of the barometer. As far as I can see I was the first who tried to explain from that conception the several phenomena.

† *Wien. Ber.* lxxiv. p. 413 (1876). Herr Goldstein has drawn no conclusion from his experiments.

‡ Wied. *Ann.* x. p. 337 (1880).

§ *Beibl.* vii. p. 725 (1883).

‖ E. Wiedemann, Wied. *Ann.* x. p. 250 (1880), and further on.

motion in the kathode-rays consequently transverse. The absorption of the kathode-rays is not, however, to be conceived as interference in the usual sense of the word, but rather as a transference of motion to other particles already moving in the same direction.

(2) Let us now turn to the property possessed by the kathode-rays, that they cannot traverse any larger layers of matter, *i. e.* to the *absorption* of the kathode-rays.

We find that every solid body, whether conductor or insulator, is absolutely opaque to the kathode-rays even in the thinnest films. Hertz (*loc. cit.*) has shown that sodium or mercury vapour introduced into the path of the kathode-rays opposed an absolute hindrance to their further progress; and he supposes that the non-appearance of the kathode-rays at higher pressures depends upon their absorption by the gas itself.

An absorption of the ultra-violet rays has been proved decisively by Cornu[*]; no experiments with hydrogen are yet at our disposal; but an increased absorption in the ultra-violet is probable on spectroscopic grounds.

It is also *à priori* probable that a general absorption of the rays of light takes place so much the more easily the smaller their oscillation-period, or the greater the number of vibrations performed during the time that the ray of light advances through a given distance. There will be an absorption if certain relationships exist between the oscillations of the æther envelopes of the molecules and those of the free æther in respect to period and direction of oscillation; it is clear that with similar conditions of the body, such will occur the more frequently the greater the number of æthereal oscillations per unit length. The strength of the absorption must, *cæteris paribus*, be proportional to the product of the number of æthereal oscillations per unit-length and the number of molecules in the unit volume. Hence the number of bodies which yield a continuous absorption-spectrum in the ultra-violet is much greater than the number of those which absorb both the visible rays and also the ultra-violet rays.

(3) With the absorption of the rays is closely connected the facility with which they produce phosphorescence and fluorescence[†], and with which they initiate chemical change.

It is this fluorescent or phosphorescent luminosity of a gas

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[*] *C. R.* lxxxviii. p. 1285 (1879); *Beibl.* iv. p. 40 (1880).

[†] The opinion of Herr Goldstein that the ends of the kathode-rays, when they strike upon a solid wall, become covered with a layer of ultra-violet light does not appear to me to be very probable.

traversed by the kathode-rays which enables us to trace the course of the rays. The æther envelopes of the gas-molecules upon which they strike are thrown into vibration and emit light. Since the kathode-rays possess in themselves very great energy, and therefore when absorbed yield up a large amount of energy, it does not appear remarkable that hydrogen in the kathode-rays shows the line-spectrum and not the band-spectrum, that in nitrogen we have a prevailing blue colour, and so on.

With strongly decreasing pressure the brilliancy of the kathode-rays decreases because the number of luminous gas-particles is lessened.

(4) We find when a negative electrode is produced, whether by directly communicating negative electricity or by connecting the wall with the earth at the point in question, and thus condensing positive electricity, that metallic electrodes generally, and the glass wall always, become covered with a luminous glow, which, upon spectroscopic examination, shows the sodium-lines and the hydrogen-lines, especially the red one, whilst in the kathode-rays themselves, as already mentioned, the blue part of the spectrum predominates. It is in the highest degree improbable, however, that there is always produced at the secondary kathodes on the way a temperature so high as corresponds to the dissociation of vapour-steam. The very lively æther motions produced at the point of origin of the kathode-rays will no doubt here also call forth primary æther motions in the solid body, which will then secondarily produce dissociation and rise of temperature. Since at the electrode itself the number of molecules is greater than in the tube, and the wall continuously absorbs energy, the gas itself can only absorb a relatively smaller amount of energy per molecule than in the free gas-space; hence here also the red hydrogen-lines are relatively brighter than in the kathode-rays themselves.

(5) The phenomenon discovered by myself[*], and called by Goldstein[†] *reflection* of the kathode-rays, is at once accounted for by the fact that they are rays of light.

(6) The " deflection " fully examined by Goldstein[‡] consists in a bending which the kathode-rays suffer when they pass near another kathode. The phenomenon is exactly similar to that which occurs when a ray of light passes near a body which is surrounded by an atmosphere the density of which decreases from within outwardly, or which is of variable

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[*] Wied. *Ann.* x. p. 236 (1880); Phil. Mag. vol. x. p. 411.

[†] Wied. *Ann.* xv. p. 246 (1882).

[‡] ' Eine neue Form electrischer Abstossung,' Berlin (Springer), 1880; *Beibl.* iv. p. 822 (1880).

pressure. In fact, in accordance with what has been explained above as to the resistance of the positive light, there exists round the electrode a space, varying from within outwards, which may very well produce such deflections in rays which traverse it.

(7) The mechanical action of the kathode-rays, such as movements of surfaces upon which they impinge, so far as they do not arise from the thermal phenomena, is seen from Maxwell's results, according to which a ray of light exerts on the wave-front a pressure which is numerically equal to the energy in the unit volume.

I have previously calculated concerning the heating which takes place at the kathode how high a value this energy may possess, of which an idea may be formed from the fact, amongst others, that in the focus of a hemispherical kathode, as is well known, platinum-foil is heated to intense glow, and glass is melted. For this last phenomenon it is important that in the highly exhausted space the heat yielded by the kathode-rays to the foil shall be given up to the surrounding air by convection only with extreme slowness.

(8) The mutual repulsion of two kathode-rays as observed by Crookes, and which, as I have been able to observe, actually occurs under the conditions which he states, *i. e.* with strong discharges and when the rays form a small angle with each other, whereas the rays cross when they meet under a larger angle, may be explained by the pressure exerted on the wave-front of the ray of light.

(9) Hertz has already (*loc. cit.*) pointed out the possible connexion of the deflection of the kathode-rays with the rotation of the plane of polarization ; without, however, expressing a definite opinion. I believe that with the above assumption as to the nature of the kathode-rays, the two phenomena will be found to be related in a definite manner.

Let S N (fig. 9) be a magnet along whose axis a ray of light is sent, vibrating, we will suppose, in the plane of the paper; then, if we place a piece of glass before the north pole, the vibrations are disturbed so that the upper part of the ray is rotated forwards.

If, now, we imagine the ray moving in a direction at right angles to the plane of the paper, instead of the direction S N, a similar rotation must take place, for the position of the æther-vibrations relative to the magnet remains unaltered. But the ray of light must always be at right angles to the direction of vibration. If, therefore, *this* be rotated, the ray of light must also be rotated, or it suffers a deflection, the ray being elevated from N onwards.

The fact that these rotations have not yet been observed in air, although with the kathode-rays they attain so high a value, may be to some extent accounted for as follows.

The rotation of the plane of polarization α is expressed, other conditions being unchanged, by the formula

$$\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \ldots,$$

where A, B, &c. are constants, and λ denotes the wave-length. α attains a greater value the smaller λ is; and it increases much more rapidly than λ does.

But this cannot be the whole of the explanation of the difference in behaviour between the kathode-rays and ordinary rays of light. If the rotation of the vibrations of light were equally great, whether it takes place in the plane passing through them and the ray of light, or in a plane at right angles to this, then this rotation could certainly be distinctly observed by placing a cylinder of Faraday's glass equatorially between the poles of a powerful electromagnet, and sending through it a ray of light coming from a slit through a collimator, and observed with a telescope provided with cross-wires. Experiments for this purpose have, however, given only negative results.

7. *On the Positive Discharge and the Formation of Stratifications.*—I propose to describe in few words a theory I have formed as to the cause of the stratifications, which affords an explanation of a series of phenomena, and with the further development of which I am now occupied.

There is formed round the negative electrode, as we have seen, a space in which the gas is in a condition altogether different from that in the rest of the tube. There is a dielectric polarization at the positive electrode, which undergoes a change when the discharge takes place: this (and not a sound-wave) is transmitted, and is followed by a current of free electricity*. When this advancing dielectric polarization reaches the neighbourhood of the kathode, it, like any other tension, is reflected, and the return-wave produces interference; the following electricity finds therefore places of maximum and minimum motion; in the first it will behave in a different way than in the latter: in the first, therefore, the gas is seen to be luminous, in the second not.

Since the anode itself must always be a point of maximum motion, it corresponds to a layer, a bright point, even when the distance of the anode from the reflecting parts of the

* Compare the conclusions in Wied. *Ann.* x. p. 245, and the reclamation of W. Siemens, Wied. *Ann.* xxix. p. 117 (1880).

kathode has become so small that no interference could take place any more; hence we find the end of the positive electrode still covered by a cap of light, even where it has broken through the last layer.

We must not, however, conceive of the point at which reflection takes place as an infinitely thin layer, but one of perceptible breadth which extends from the boundary of the bright kathode-layer on the side of the kathode to the positive light. The broader this layer becomes, the broader must also be the places of maximum motion, and conversely: thus we find with high pressures and a narrow bright kathode-layer, well-defined narrow stratifications; with low pressures and broad kathode-layer, the stratifications are diffuse; the distribution of light in the stratifications is also explained.

If too large quantities of electricity accumulate on the anode, or if the current is too rapid, then, in consequence of the irregular motion, no stratifications are formed.

The idea of Herr Goldstein that each separate layer behaves as a conducting element with anode and kathode, seems to me to be only a mode of describing certain phenomena observed in the stratifications, but not to furnish an explanation of them. The anode and kathode of a layer would, in this way of regarding the matter, have to be considered as the points of entrance and exit of electricity in layers of gas in a peculiar condition of motion or of tension.

It might be supposed that certain difficulties would present themselves to this explanation, in cases where the positive electrode is in connexion with the earth, and the negative connected with the source of electricity.

I am inclined to think that the phenomena in this case may be explained as follows. Under the influence of the electricity accumulated on the negative electrode, or of positive withdrawn from it, there is produced a dielectric polarization starting from the luminous kathode-layer surrounding it. The high resistance which experiment shows to exist is opposed by the dark kathode-layer to the neutralization of electricity in the direction of the negative electrode. The dielectric polarization therefore spreads out towards the positive electrode, where occurs a condensation of free electricity. As soon as its tension has risen sufficiently, the discharge occurs in the manner described above. The much more regular formation of stratifications observed in this case has its ground in the small quantity of free electricity accumulated upon the positive electrode, which flows off much more regularly than when new quantities of electricity pass continually from the source of electricity to the electrode.

8. *Further Observations upon the Influence of the Magnet upon the Discharge.*—A series of measurements and observations were made upon the behaviour of the discharge under the influence of feeble magnets. These have led to results which partly differ from those of previous observers, partly complete them.

I employed for these experiments a tube 25 millim. wide and 410 millim. long, with plate-electrodes which had been highly exhausted.

The kathode *k* (fig. 3) was insulated and connected with the negative pole; the electrode *a*, on the other hand, was connected with the earth by a long moist thread, as well as to the positive pole of the machine. A dark space appeared about *k*, which extended to *b*; this was traversed by the kathode-rays, which issued in a narrow, slightly divergent pencil from the centre of the plate *h*. Up to the middle of the space *h b* these were of a white colour; but afterwards more of a blue colour. From *b* itself issued from the whole surface of the corresponding kathode-layer a bluish luminosity — the "glow-rays," through which the kathode-rays could be traced. Three or four cloudy stratifications were visible about *a*. The tube showed from *b* to *a* a bright-green light on the walls, so that here also the peculiar kathode-rays penetrate the positive light without meeting with any hindrance whatever, and the positive light can also diffuse itself through the kathode-rays unhindered. If the one pole of a bar-magnet be brought near such a tube, green light becomes visible on the wall, which shows that the kathode-rays and the blue "glow-light" are, as we know, so deflected that a north pole placed under the tube throws them to the right, if we are looking from the positive electrode towards the negative.

But these phenomena are seen still more clearly if, instead of a bar-magnet, we employ a horseshoe-magnet with poles as close to each other as possible (best a small lamellar magnet of Jamin's construction), placing it so that the tube occupies the equatorial position.

We must distinguish two cases:—(1) Both poles of the magnet produce a deflection of the discharge, such that the " glow-light " and the kathode-rays are deflected on each side towards the walls; or (2) both poles deflect the rays towards the centre of the tube.

(1) In the first case, if the magnet is placed between the anode and the boundary of the dark space, there is seen on the wall a green spot of light bounded by two ellipses. These ellipses are produced by planes intersecting the tube and inclined to its axis. The form is that represented in fig. 10; *c* is the luminous surface, *a f* and *b d* its boundaries. The boun-

dary furthest from the negative electrode is the brighter, but
both are equally sharply defined. The line of light db does
not reach quite to the end of af, but cuts this line. Also the
line af does not extend quite round the tube, but ends where
the magnet is, bending a little so as to become more nearly
parallel to the axis of the tube. If the magnet is moved from
the anode towards the kathode, the two boundaries approach
each other the more closely the nearer the magnet comes to the
negative electrode, until at last they coincide. Notwithstanding,
so long as the magnet-pole is not close to the limit of the dark
kathode-layer (in one case so long as it was not nearer than
about 12 millim.), the inclination of the green ring to the axis
of the tube from the positive electrode remains constant, and
in the above case amounted to $\tan^{-1}\frac{25}{50}$. But if the magnet
approaches the dark layer, the inclination decreases consider
ably, and at the boundary of the dark space attains the value
$\tan^{-1}\frac{25}{90}$. When the magnet-pole has somewhat overpassed
the limit of the dark kathode-space, the luminous figure
becomes indistinct, reducing itself to a spot of light, and this
recedes further from the pole as the magnet approaches the
electrode.

The phenomenon appears at all pressures within certain
limits. The distance of the magnet from the electrode, beyond
which the deflection is of such a nature that the half-moon
shaped figures are produced, is greater the greater the exhaus-
tion, evidently because the dark space extends continually
further and further.

If we examine the deflection of the kathode-rays more closely,
we find that it only takes place from the point where the white
colour changes into blue. But since the deflection of the ring
is so much dependent upon the position of the magnet relative
to the electrode, and there is scarcely any ring formed when
the magnet is behind the limit of the glow-light, we see that the
kathode-rays behave altogether differently within the dark
space. And when they have once traversed it they offer, in
the first position, a much greater resistance to all lateral dis-
placement.

It is very probable that the glow-rays which are beyond the
dark space play some part in the formation of the green ring.

(2) In the second case, where both magnet-poles a and b
deflect the rays towards the centre so that they are there com-
pressed, there appears a bright strip of light which, starting
from the line joining the poles, extends towards the positive

electrode. Its form is somewhat that of fig. 11. It is sharply
defined from the neighbourhood of the magnet to δ, where its
two bounding lines meet; from there on, it is accompanied by
somewhat diffused light.

The phenomenon also appears most distinctly when the
magnet-poles are at some distance from the kathode. Peculiar
phenomena are observed when, having produced the sickle-
shaped figure by means of a magnet placed under the tube, we
bring the one pole of a bar-magnet near to the tube from above.
The inner, weaker border undergoes only slight displacement,
but the outer, stronger border is greatly deformed. The con-
tour is shown in fig. 12: . . . . shows the weaker boundary nearest
the kathode, - - - - the stronger boundary seen upon the wall of
the tube. The portion *n m* was, to begin with, upon the same
side of the tube upon which it still is; but the portion *m l* is
bent over from the other side of the tube, and has thus experi-
enced a rotation of nearly 180°.

The weaker boundary is therefore produced by rays which
resist bending and deflection much more than those which
produce the stronger boundary.

In the above description no notice has been taken of the
behaviour of the positive column of light. We turn now to
consider it.

If we move the Jamin magnet, in its equatorial position,
along the tube from the positive pole, the stratifications preserve
their position almost unaltered, although the green ring is
already visible, until the centre of the plane passing through
the ring cuts the first layer. At this moment it disappears,
uniting with the second; so that this becomes the first. This
itself then gradually advances with the magnet, and indeed
in proportion as the glow-rays are bent to the side, while new
layers continually appear from the anode. If we move the
magnet backwards, we find that the first layer divides as soon
as it has passed the ring.

In most cases the persistent first anode-layer, as described
above, appears under the influence of the magnet. In some
cases, under conditions which I have not been able completely
to determine, we observe a simple displacement of the first
layer, whilst, however, there was always noticed a consider-
able expansion, *e. g.* with retrograde motion of the magnet,
corresponding to the previously mentioned division, and sub-
quent shortening of the layer.

If the magnet in its motion reaches the limit of the dark
space, the first positive layer remains stationary for a moment;
and then, upon a further approach of the magnet to the kathode,
retreats, whilst at the same time the kathode-rays and glow-

rays penetrate further into the tube, thus conditioning the first phenomenon.

The usual description of the phenomenon, according to which the positive-light column is simply attracted to the magnet, whilst new stratifications continually disengage themselves from the positive electrode, whilst the first remains unchanged and moves toward the kathode, therefore does not always apply.

9. *Behaviour of Poor Conductors as Kathodes.*—A few experiments relate to the behaviour of bad conductors as kathodes. The questions to be decided were, first of all, whether such poor conductors would be disintegrated in the same way as good conductors, whether kathode-rays would appear, &c. Paper and similar substances have been previously employed as poor conductors, and the electrodes have been covered with these substances. I have not employed these substances; for so long as they are not perfectly dry, no vacuum at all perfect can be obtained with them; and if they are perfectly dry, they are insulators which can only be broken through in disruptive discharges. ⸻

I have therefore used lead chloride and lead iodide, which at ordinary temperatures conduct very badly. In order to cover the electrodes with these substances, the discharge-tube was made of the form shown in fig. 13. An aluminium electrode is melted into one end of the tube in the ordinary manner, whilst at the other end at d a narrow tube was melted on. In this a still smaller glass tube δ fitted exactly. A platinum wire was melted into one end α, into which a drop of mercury (β) was brought; and an aluminium wire (γ) was pushed into the tube and dipped in the mercury. In the part ϵ of δ not occupied by the aluminium wire, chloride or iodide of lead was melted until the space ϵ was completely filled, when the tube δ was pushed into the tube c and cemented with sealing-wax. The electrode is completely covered by glass and not by cement, so that it does not need further melting in. This arrangement may be recommended, *mutatis mutandis,* for the construction of other forms of discharge-apparatus.

With chloride or iodide of lead fine kathode-rays were obtained accompanied by a very decided deposit upon the walls, and especially upon the parts within the dark space round the kathode, although the kathode-rays traversed the tube altogether in the line of the axis. This deposit showed Newton's rings plainly, and formed very rapidly. Whether its formation is attended by electrolytic decomposition of the lead-salt remains to be investigated. When iodide of lead is used, peculiar spectral phenomena are observed, the description of

which must be reserved for a later paper. We see thus that kathodes formed of poor conductors do become disintegrated.

10. *Dependence of the Potential of Discharge upon the Form of the Electrode.*—A series of experiments were made to determine in particular tubes how the potential necessary to initiate the discharge depends upon the form of the electrodes. All the tubes were of the same size, 25 millim. wide and 120 millim. long. The first tube contained two plates, the second two points, and the third a point and a plate at a distance apart of 58 millim.

The first result obtained was that, if the three tubes are connected with the positive and negative poles of the machine side by side at pressures exceeding 1 millim., the discharge passed only in the tube with the points; at lower pressures only in that with the plates.

A second mode of experiment consisted in using one tube only, but including a spark-micrometer in a second parallel circuit, and then gradually separating the balls of the micrometer until the discharge passed through the tube, or by bringing the balls nearer to each other from a considerable distance until the discharge took place between the balls. In the last case the distance is always greater than in the first, partly because the discharge between the balls of the micrometer takes place more easily when the air between them has been heated and rarefied by the stream of sparks, and partly because the walls of the glass tube become charged; and it therefore requires a higher potential to produce the first discharge through the tube than is necessary for the following ones.

The experiment showed next that connecting either of the electrodes with the earth is without any important effect.

At very low pressures the following results were obtained:—

(1) With the tube with two points the spark-distance might be increased to 9 millim. without the discharge taking place. (2) With the tube with one plate and one point, if the plate was negative, no discharge took place in the tube, even when the spark-distance amounted to 11 millim.; but if the plate was positive, the discharge occurred at a distance of 3 millim. (3) If both electrodes were plates, discharges took place at a spark-distance of 2 millim.

Hence it follows that a greater potential is necessary for the discharge between two points than between two plates, and that part is taken not only by the negative electrode, but also by the positive.

An altogether peculiar phenomenon manifests itself if we employ a tube of the form shown in fig. 14, making the small

electrode α, cut off close to the glass, the kathode, and the large electrode the anode: a pencil of kathode-rays issues from the point of the kathode; and we find also the glass tube surrounding it shows bright-green fluorescence, as if the wall of the tube about α had become a kathode. The explanation is to be found in the fact that the electricity issuing from the anode cannot make its way through the small surface of the kathode, and flows towards the wall about α, which therefore acts as a kathode.

11. *Remarks upon the Management of Electrophoric Machines.*—With the consent of Herr Hofrath and Dr. Töpler, I add the following remarks:—When an electrophoric machine has been used for a long time, it often becomes useless on account of the dust deposited upon it and burnt into the layer of varnish; and this has to be renewed, which is troublesome, and does not always answer, since the glass of the plates themselves is often attacked. Herr Töpler proposes to cover the plates with a layer of paraffin, which can easily be prepared and renewed. The fixed plates are dipped into melted paraffin contained in a tin vessel large enough to take the plate. In order to cover the rotating plates, a tin vessel is used into which three or four can be plunged up to the centre, filled with melted paraffin, and the plates plunged in while they are rotated, without being removed from the axle. It is advantageous to heat the plates as much as possible before dipping them in, by means of the heating-apparatus provided with the machine, in order to avoid all risk of the plates cracking. The superfluous paraffin is removed by rapid rotation of the plates after removal from the paraffin-bath.

If after long use the plates become dusty again and covered with metallic particles from the points, it is sufficient to heat them on the machine so as to melt the paraffin and cover up the dust. After a long time an entire renewal of the paraffin will be necessary.

In working for a length of time with electrophoric machines, it is not advisable to have them in the laboratory. Ozone is a poisonous gas, and is the more dangerous because its evil effects are not perceived at once; on the contrary, breathing it appears at first to be attended by increased animation, but afterwards it produces evil effects upon the nervous system. Thus Binz[*] has shown that it produces sleep.

My best thanks are due to Mr. Cole, of Cambridge, U.S.A., who has assisted me in these experiments with the greatest zeal.

[*] *Berl. Klinische Wochenschrift*, No. 1, ii. p. 40 (1882).

XI. *On a Method of Measuring the Electrical Capacity of a Condenser, and on the Determination by Electrical Observations of the Period of a Tuning-fork.* By R. T. GLAZE-BROOK, *M.A., F.R.S., Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge*[*].

THE experiments described in the following paper were undertaken at the request of Messrs. Latimer Clark, Muirhead, and Co., for the purpose of testing one of their condensers "which," quoting from a letter from the firm, "has lately been made and which we use in the factory. In its construction it is the same as all our condensers, and is made of sheets of mica and tinfoil and laid with paraffin-wax."

The method employed was a modification of one given by Maxwell (vol. ii. § 776), and used by J. J. Thomson (Phil. Trans. iii. 1883) in his recent determination. The following is his description of the arrangement :—

"In a Wheatstone bridge, A B C D (fig. 1), with the galva-nometer at G and the battery be-tween A and B, the circuit B D is not closed, but the points B and D are connected with two poles, R and S, of a commutator, between which a travelling piece, P, moves back-wards and forwards. P is connected with one plate of a condenser, the other plate of which is connected with D. Thus, when P is in con-tact with S the condenser will be charged, and until it is fully charged
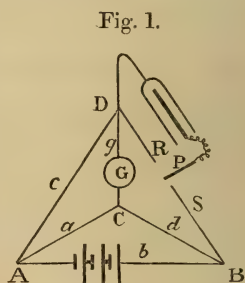
Fig. 1.

electricity will flow into it from the battery : this will produce a momentary current through the various arms of the bridge. When the moving piece P is in contact with R, the two plates of the condenser are connected, and the condenser will dis-charge itself through D R ; and as the resistance of D R is infinitesimal in comparison with the resistance in any other circuit, the discharge of the condenser will not send an appre-ciable amount of electricity through the galvanometer. Thus, if we make the moving piece P oscillate quickly from R to S, there will, owing to the flow of electricity to the condenser, be a succession of momentary currents through the galvanometer. The resistances are so adjusted that the deflection of the gal-vanometer produced by these momentary currents is balanced

by the deflection due to the steady current, and the resultant deflection is zero. When this is the case, there is a relation between the capacity of the condenser, the number of times the condenser is charged and discharged in a second, and the resistances in the various arms of the bridge."

The investigation given by Maxwell is only approximate ; we shall quote therefore the result given in Thomson's paper.

Let a be the resistance of A C,
$\quad b \quad$,, $\quad$,, $\quad$ A B,
$\quad c \quad$,, $\quad$,, $\quad$ A D,
$\quad d \quad$,, $\quad$,, $\quad$ B C,
$\quad g \quad$,, $\quad$,, $\quad$ D C.

Let C be the capacity of the condenser, n the number of times it is charged and discharged per second ; then

$$nC = \frac{a\left\{1 - \dfrac{a^2}{(a+c+g)(a+b+d)}\right\}}{cd\left\{1 + \dfrac{ab}{c(a+b+d)}\right\}\left\{1 + \dfrac{ag}{d(a+c+g)}\right\}}.$$

The commutator was the one used by J. J. Thomson, and we will quote his description :—" The current from some Grove cells passes first through a tuning-fork interrupter and then through the coils L M (fig. 2) of an electromagnet.

Fig. 2.
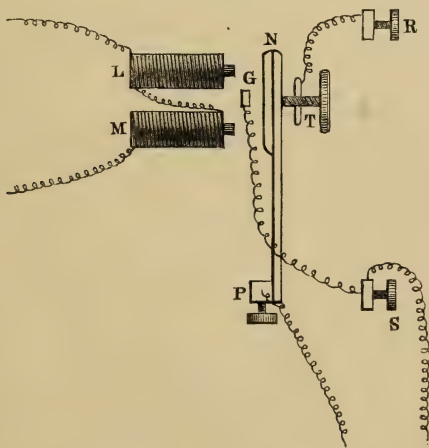
P N is a strip of brass with a piece of iron wire attached to it. When there is no current passing through the electromagnet,

the elasticity of the rod P N makes it press against the
screw T, which is electrically connected with the binding-
screw R. When the current passes through the electromagnet,
the magnet attracts the iron attached to the rod P N and
brings it into connexion with the stop G, which is electrically
connected with the binding-screw S. The letters P R S indi-
cate the same points in this figure as in fig. 1. All the places
where contact is made are covered with platinum, and the
whole arrangement is fastened down to an ebonite board. As
the current passes intermittently through the coils L M of the
electromagnet, the vibrating-piece P N strikes alternately
against the parts G and T. When it strikes against G, the
opposite plates of the condenser are connected with the two
poles of the battery; when it strikes against T, the condenser
is discharged."

The main advantages of this method over the one ordinarily
employed for the determination of the capacity of a condenser
whose capacity is comparable with a microfarad are easily
seen. In the first place it is a null method; no assumptions
are required as to the constancy of the battery. In the
second, the galvanometer can readily be made much more
sensitive. For accurate work in the ordinary method, the
field of force in which the galvanometer-needle hangs should
be nearly uniform. The earth's force is much too strong,
unless an enormous battery-power be employed, and it is
difficult to secure a uniform field by a control magnet.
Something may of course be done by the use of an astatic
galvanometer-needle; but it is impossible to increase the
sensitiveness in this way very much, because the torsion of the
suspending fibre then becomes important. Again, in the
ordinary method the time of swing cannot be determined
accurately if it be made too small; the moment of inertia of
the suspended parts therefore must be considerable, and the
deflection produced by a given quantity of electricity suddenly
discharged through the galvanometer is proportionately de-
creased; for, if T be the time of swing, θ the throw produced
by a quantity of electricity Q, then T $\sin \frac{1}{2} \theta$ is proportional
to Q. In addition to this, there is the correction for damping
which has to be considered.

On the other hand, objections may be raised to the method
which has just been described. The most important of these
is founded on the fact that the time during which the plates
of the condenser are in contact either with each other or with
the poles of the battery is very short. It may happen, then,
that the condenser is neither charged nor discharged com-
pletely at each vibration of the commutator; while if there be

any electrical absorption in the condenser, its effects will depend on the time during which the contact lasts. The experiments to be described were undertaken with the view of testing the method for these defects. The time during which the plates of the condensers are connected with the battery is the time during which the spring P N is in contact with G. This is only a fraction of the period of the tuning-fork which governs the commutator, a fraction which depends on the distance between the end of the screw T and the point G, and on the strength of the current in the electromagnet.

A series of experiments were made to test the effect of varying the position of the screw T, keeping the battery the same. In these, four Leclanché cells were used in the battery-circuit A B, and two pint Groves to drive the commutator. The position of the spot of light on the scale was noted, and then the value of the resistance *d* adjusted until no deflection was produced when the galvanometer-circuit was closed by means of a key.

The commutator, when working correctly, emitted a definite sound which was readily recognized; and it was found that the screw T could be adjusted within certain limits without altering this sound.

Table I. gives the results of these observations.

Table I.

Commutator adjustments.	Value *d* in B.A. units.
Screw T set....................................	905
Screw T readjusted, note good	906
,, ,, ,, ,, ...	906
,, ,, ,, bad	906
,, ,, ,, good	906
Screw T loosened one turn. Spot off scale.	
Screw T readjusted, note good ....,......	906

Thus the value of *d* required to give a balance is practically the same throughout, and the commutator with a definite battery-power can readily be set to give a definite result; moreover, a balance could never be obtained except with the resistance 905 or 906. In the fourth observation the note of the commutator was marked as bad; but the spot remained stationary, showing that though there seemed to be a slight irregularity in the sound, it was too small to affect the balance. The sensitiveness was such that an alteration in *d* of 1 B.A. unit produced a deflection of from two to three scale-divisions. The number of vibrations of the fork was about 32 per second.

Another set of observations was then taken to test the effect of varying the battery-power driving the commutator, thus altering the force with which the spring P N is attracted to G, three Grove cells being used in place of two. The values of *d* found in two separate observations were 905·5 and 905.

Observations were made to test the effect of varying the period of the driving-fork. Forks of frequencies of approximately 16, 32, 64, and 128 to the second were taken, and the pitch of the lowest of these determined absolutely by comparison with the clock in the method described by Lord Rayleigh ('Nature,' xvii. p. 12; Phil. Trans. 1883, Pt.I.). This fork and the 32 fork were then set going on independent circuits, and a pointer attached to the 32 fork was watched over the top of a plate of thin metal which had been all along fixed on to the 16 fork, the eye being placed so that this pointer was visible for only one position of the 16 fork in each vibration. In this way the beats between the octave of the 16 fork and the 32 fork were visible, and could easily be counted.

Thus the period of the 32 fork was found, and then in a similar manner those of the 64 and 128 forks. By loading with wax one of the two forks under comparison, it was easy to find which of the two was gaining.

Each of these forks was used in turn to drive the commutator, and the value of the capacity calculated from the observations. The values of the resistances were as follows:—

a was a standard coil of 10 B.A. units, *d* a resistance of 1000 B.A. units, taken from a box by Messrs. Elliott, Bros., and *c* a variable resistance from another box by the same firm.

g, the galvanometer-resistance, was about 11,000 B.A. units; and *b*, the battery-resistance, from 5 to 6 B.A. units. The galvanometer-resistance was higher than necessary, but it was for other reasons the most convenient instrument for the purpose. The value of *c* varied from about 1800 to about 240 B.A. units.

It will be found that, with these values, the equation giving the capacity may be written

$$n\mathrm{C} = \frac{a}{cd\left\{ 1 + \dfrac{a}{d\left(1 + \dfrac{c}{g}\right)} \right\}}.$$

[The approximate equation given in Maxwell is

$$n\mathrm{C} = \frac{a}{cd}.]$$

We shall use N_{16} &c. to denote the frequency of the fork of approximate frequency 16.

The following are the results of the observations :—

(1) Fork 16 used.

Fork compared with pendulum. Fork loses 1 vibration in 7·46 seconds.

$$N_{16} = 15 \cdot 866 \text{ sec.}$$

Resistance observation :—

$$a = 10; \quad d = 1000; \quad c = \begin{Bmatrix} 1895 \\ 1892 \\ 1893 \end{Bmatrix} 1893 \text{ mean.}$$

Sensitiveness 1 scale-division for alteration of 1 B.A. unit in c.

From these we find

$$C_{16} = \cdot 3300 \, \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(2) Fork 32 used.

16 beats occur in 42 seconds between octave of 16 and 32. Fork 32 gaining.

$$N_{32} = 32 \cdot 11.$$

Resistance observations :—

$$a = 10; \quad d = 1000; \quad c = \begin{Bmatrix} 934 \\ 934 \\ 934 \end{Bmatrix} 934 \text{ mean.}$$

Hence

$$C_{32} = \cdot 3304 \, \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(3) Fork 64 used.

10 beats occur between 64 and octave of 32 in 50 seconds. Fork 64 gaining.

$$N_{64} = 64 \cdot 42.$$

Resistance observations:—

(α) $\qquad a = 10; \quad d = 1000; \quad c = 466;$

$$C_{64} = \cdot 3299 \, \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(β) $\quad a = 10; \quad c = 1000; \quad d = \begin{Bmatrix} 461 \\ 461 \cdot 5 \end{Bmatrix} 461 \cdot 3 \text{ mean.}$

$$N_{64} = \cdot 3299 \, \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(4) Fork 128 used.

16 beats occur between the 128 fork and octave of 64 fork in 26·25 seconds. Fork 128 gaining.

$$N_{128} = 129 \cdot 05.$$

Resistance observations:—

$$a = 10 \; ; \quad d = 1000 \; ; \quad c = 232 \cdot 5.$$

Hence
$$C_{128} = \cdot 3301 \; \frac{\text{ohm}}{\text{B.A. unit}} \; \text{microfarad.}$$

The sensitiveness throughout these observations was such that an alteration of 1 in 2000 in the resistance produced a deflection of about one scale-division in the spot of light.

Hence the greatest difference in the observations amounts to about 5 in 3300, or about 1 in 660 ; and there is no trace visible of variation in the capacity with the time of charging.

We will collect the numbers together:—

$$
\begin{aligned}
&C_{16} \; \dots\dots\dots\dots\dots\dots\dots\dots\dots \; \cdot 3300 \\
&C_{32} \; \dots\dots\dots\dots\dots\dots\dots\dots\dots \; \cdot 3304 \\
&C_{64} \; \dots\dots\dots\dots\dots\dots\dots\dots\dots \; \cdot 3299 \\
&C_{64} \; (\text{second arrangement})\dots\dots \; \cdot 3299 \\
&C_{128} \dots\dots\dots\dots\dots\dots\dots\dots\dots \; \cdot 3301
\end{aligned}
$$

Mean value of capacity $= \cdot 33006 \; \dfrac{\text{ohm}}{\text{B.A.U.}}$ microfarad.

Taking the Cavendish-Laboratory experiments, we have

$$1 \; \text{B.A. U.} = \cdot 9867 \; \text{ohm.}$$

$$\therefore \quad C = \frac{\cdot 33006}{\cdot 9867} \; \text{microfarad}$$

$$= \cdot 3344 \; \text{microfarad.}$$

If we take the legal ohm and the value of the specific resistance of mercury in B.A. units, adopted by the B.A. Committee,

$$1 \; \text{B.A. unit} = \cdot 9889 \; \text{ohm,}$$

and
$$C = \cdot 3336 \; \text{microfarad.}$$

This value supposes that the various coils used have their nominal resistance in B.A. units. And this assumption is correct, at any rate to 1 in 1000. Thus it seems that the method gives satisfactory results, and may safely be used to determine the capacity of a condenser.

But the converse of the method may be even more useful. The fundamental equation gives us C if we know n and the resistances; it will equally give us n if we know C and the resistances; and in many cases this may be the readiest method of finding n, especially if the period is too long to give an audible note. Thus in the above experiments I require to adjust a fork to vibrate about 16 times a second, the lowest I could obtain being one of a frequency of almost 20.

I made observations with the 32 fork, the pitch of which was marked on it by the maker, of the value of *c* required to produce a balance, then doubled this value of *c*, and set the fork which it was required to adjust to drive the commutator. Leaden weights were then fixed with screws on to the prongs of the fork, and their position was adjusted until the galvanometer-balance was not disturbed on making contact. It was clear, then, from the approximate formula that the frequency of the fork was very nearly 16. And on making the comparison with the clock, it was found to be 15·866, as already stated.

My thanks are due to Messrs. Wilberforce, Whitehead, and Fitzpatrick for assistance in making the experiments.

XII. *On Salt-Solutions and Attached Water.*—VIII.
By Frederick Guthrie.

§ 242. *T*HERMAL *Relation of some Aniline Salts to Water.*— In turning to organic ammonias and their salts which contain radicals of greater molecular weight, and belonging to different series from those we have been considering above, we are tempted by aniline. It can be got in a state of great purity. Its salts are well defined and stable, and of various degrees of solubility. The aniline I employed was rectified several times, converted into the chloride, and twice recrystallized; reconverted into the base by caustic potash, dried, and finally distilled.

Aniline is slightly soluble in water. On cooling to a temperature of − 0°·7, the water and aniline solidify together as a porcelain-like opaque cryohydrate, which is, however, too poor in aniline to be capable of satisfactory analysis.

§ 243. *Chloride of Aniline.*—As a cryogen, the chloride of aniline gave a temperature of −10°·5. For its solubility the weighed solution was evaporated in a water-bath until it ceased to lose weight. Saturated at 13°·1, it was found that 8·3210 grams gave 3·8875 anhydrous salt, or 46·72 per cent. Saturated at 0°, 13·2836 grams gave 5·3595 grams dry salt, or 40·35 per cent. The solution saturated at 0°, or a 20-per-cent. solution placed in a freezing-mixture, falls to the temperature of −10°·7. It is here as generally preferable to reach the cryohydrate from the dilute side. This cryohydrate readily forms a supersaturated solution. Of the cryohydrate, 7·1760 grams gave 2·2860 dry salt, or 31·86 per cent.

Percentage solutions were then made, and their temperatures of initial solidification determined.

TABLE L.

Chloride of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	− 0·2 C.	Ice.
4	96	− 1·0	,,
5	95	− 1·3	,,
6	94	− 1·6	,,
7	93	− 1·9	,,
8	92	− 2·2	,,
9	91	− 2·5	,,
10	90	− 2·8	,,
11	89	− 3·0	,,
12	88	− 3·3	,,
13	87	− 3·6	,,
20	80	− 5·7	,,
25	75	− 7·2	,,
30	70	− 9·0	,,
31·86	68·14	−10·7	Cryohydrate.
35	65	− 8·0	Salt.
40·35	59·65	0	,,
46·72	53·28	+13·1	,,

The curve corresponding to the above table is shown in fig. 2.

§ 244. *Nitrate of Aniline.*—As a cryogen, the temperature −2°·2 was obtained. A solution saturated at 13°·1 was evaporated *in vacuo* over sulphuric acid until it ceased to lose weight; 7·5174 grams gave 1·1710 gram dry salt, or 15·58 per cent. 8·6860 grams of solution saturated at 0° gave 0·9500 gram, or 10·94 per cent. A dilute solution reached, in a freezing-mixture, the constant temperature of −2°·2. Of this, the cryohydrate, 7·7972 grams gave 0·8270 gram dry salt, or 10·61 per cent. The nitrate cannot be dried in a water-bath without suffering partial decomposition. The above results are embodied in the following table, which also shows the temperatures of initial solidification.

TABLE LI.

Nitrate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
2	98	− 0·4	Ice.
4	96	− 0·8	,,
6	94	− 1·1	,,
8	92	− 1·5	,,
10	90	− 2	,,
10·61	89·39	− 2·2	Cryohydrate.
10·94	89·06	0	Salt.
15·58	84·42	+13·1	,,

Fig. 2 shows the curve representing the above numbers.

§ 245. *Sulphate of Aniline.*—This salt was recrystallized three times, and after drying between blotting-paper was finally dried before a brisk open fire. As a cryogen it showed a temperature of $-0°\cdot8$. Of the solution saturated at $13°\cdot1$, it was found that $25\cdot6925$ grams gave $1\cdot5000$ dry residue, or $5\cdot84$ per cent. Of the solution saturated at $0°$ C., $8\cdot8675$ grams gave $0\cdot4357$ gram, or $4\cdot91$ per cent. The solidifying temperature of the cryohydrate was found to be $-0°\cdot9$, and $9\cdot5607$ grams of it gave $0\cdot4620$ gram dry salt, or $4\cdot83$ per cent. This salt appears to melt in its water of crystallization, and takes a long time to dry. The following table contains the above results, together with the temperature of initial solidification in solutions of several strengths. The sparing solubility of the salt limits the table very much.

TABLE LII.

Sulphate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	$- 0\cdot1$	Ice.
2	98	$- 0\cdot2$	,,
4·5	95·5	$- 0\cdot6$	,,
4·83	95·17	$- 0\cdot9$	Cryohydrate.
4·91	95·09	0	Salt.
5·84	94·16	$+13\cdot1$	,,
15·35	84·65	$100\cdot0$	,,

The curve representing this table is found in fig. 2.

§ 246. *Oxalate of Aniline.*—$8\cdot3230$ grams of the oxalate of aniline saturated at $14°\cdot5$ gave $0\cdot1080$ gram dry salt, or $1\cdot29$ per cent. At $0°$ I obtained $0\cdot0320$ gram of the dry salt from $10\cdot8170$ grams solution, which means only $0\cdot29$ per cent. The cryohydrate was formed at the very high temperature of $-0°\cdot4$. On evaporation, $8\cdot5450$ grams gave $0\cdot02$ gram dry salt, or only $0\cdot14$ per cent. The sparing solubility of the salt in water prevented me from examining solutions of strengths weaker than the cryohydrate.

TABLE LIII.

Oxalate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
0·14	99·86	$- 0\cdot4$	Cryohydrate.
0·29	99·71	0	Salt.
1·29	98·71	$+14\cdot5$	,,

For curve see fig. 2. Although the temperature here shown for the cryohydrate is distinctly below zero, proving that the oxalate is not, like a colloid, molecularly free from the water, yet I am not assured that I have been able to form a true cryohydrate in the solid form. The ice and salt separate apart, the former adhering to the glass, and the microscopic transparent crystals of the latter remaining in suspension in the solution. The first analysis, indeed, showed greater percentage of salt at $-0°\cdot4$ than at $0°$, the difference amounting to about $0\cdot28$ per cent. on the highest. This is an impossible result. The state of things clearly arose from the circumstance that the liquid cryohydrate was enriched by the suspended crystals. The solution at $0°$ was also abnormally rich from the same cause. It was only on keeping the solution in ice for twenty-four hours that the zero amount above given was obtained, and by keeping the zero solution for twelve hours in a weak freezing-mixture (nitre and ice) that the cryohydrate (in a liquid form) was got.

§ 247. *Salicylate of Aniline*[*].—The above remarks are again applicable to this salt. So sparingly is it soluble in water at all temperatures, and so close below $0°$ is the cryohydrate, that no examination of this region was practicable. Of a solution at $0°$, $10\cdot3720$ grams gave $0\cdot0295$ gram, or $0\cdot28$ per cent. The cryohydrate formed at $-0°\cdot05$ or $-0°\cdot07$. Of it, $10\cdot0310$ grams gave $0\cdot0245$ gram, or $0\cdot24$ per cent. A solution saturated at $6°\cdot2$ gave $0\cdot0710$ gram salt out of $10\cdot9270$ grams solution, that is $0\cdot65$ per cent. Even at $16°\cdot8$ there was only obtained $0\cdot0800$ gram from $10\cdot3450$ grams, or $0\cdot77$ per cent.

TABLE LIV.

Per cent. of salicylate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
0·24	99·76	$-\overset{\circ}{0}\cdot06$	Cryohydrate.
0·28	99·22	0	Salt.
0·65	99·35	$+ 6\cdot2$	,,
0·77	99·63	$+16\cdot8$	,,

For the graphic representation of these numbers see fig. 2.

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[*] The salicylate of aniline has not, I believe, been previously described. It is obtained by mixing an alcoholic solution of aniline with the acid. It fuses at about $150°$, and cannot be distilled without decomposition. It is slightly soluble in bisulphide of carbon; soluble in ether, hot or cold; soluble in alcohol, hot or cold; soluble in hot benzol, very sparingly in cold.

§ 248. *Pyrogallate of Aniline**.—3·7270 grams of the solution saturated at 17°·8 yielded 1·7440 gram dry salt *in vacuo*, or 46·80 per cent. Of a solution saturated at 0° C., 5·92 grams gave 1·992 gram of the dry salt, or 33·65 per cent. As a cryogen the temperature −4°·6 was obtained, and the cryohydrate showed the same temperature. 9·397 of cryohydrate gave 2·253 of salt, or 23·98 per cent. The above results, and the separation of solid matter on loss of heat, are exhibited in the following table :—

TABLE LV.

Per cent. of pyrogallate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
9·09	90·91	− 1·0	Ice.
20·00	80·00	− 2·7	,,
23·98	76·02	− 4·6	Cryohydrate.
33·65	66·35	0	Salt.
46·00	54·00	+17·8	,,

The curve corresponding to these numbers is found in fig. 2. It is to be noted that amongst all the curves referring to the aniline salts, that belonging to the nitrate alone has a well-marked concavity on its ascending branch (from the cryohydrate to the right) turned towards the axis of strength. The very important signification of this curvature will form the key to much in the next Chapter referring to the limit of solubility, or rather to the unlimited solubility in certain cases of certain salts, especially nitrates.

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* As I do not find any account of this body, I may briefly note its preparation and properties. On mixing the two substances pyrogallic acid and aniline, a dry hard mass is obtained. As this is soluble in aniline, only a slight excess of the latter is used. The solid mass is dissolved in a minimum of hot benzol ; cooled to about 5°, filtered, and washed with cold benzol. Amongst its properties are the following :—It fuses at 126° C. or 128° C. It is very soluble in water, hot and cold ; also in hot and cold alcohol and ether ; soluble in hot benzol, very sparingly in cold ; very sparingly soluble in bisulphide of carbon, hot or cold. Fused on glass, it forms a beautiful crystalline film, the crystals being several inches long. It is anhydrous. In another preparation, 1 part of pyrogallic acid was dissolved in 4 parts of water at 50°. Aniline was added until a specimen became cloudy on cooling. It was cooled to about 10° and filtered through wet paper. It was then evaporated to about half its bulk and dried *in vacuo* over sulphuric acid. It turns brown on exposure to the air.

Fig. 2.—Aniline Salts.
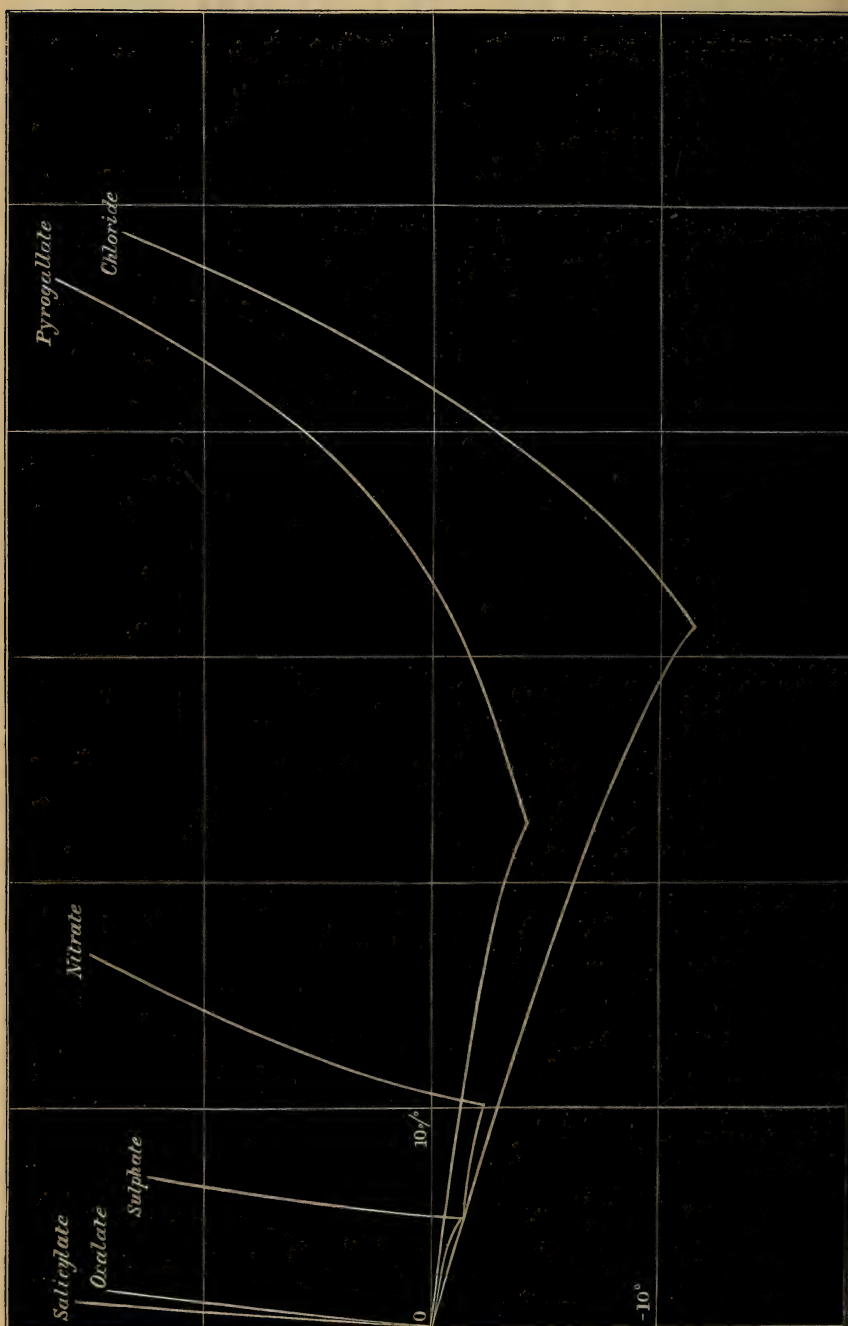
Infinite Solubility.

§ 249. An examination of curves of solubility of salts in water, drawn so that the ordinates are temperatures and the abscissæ are percentages, reveals two types of curves, which differ only essentially in their right-hand or salt-saturated branches. Iodide and bromide and, perhaps, chloride of sodium may be taken as the type of *a*, fig. 3, and nitre of *b*, fig. 3 (see § 126). The curvature of the right-hand branches of both curves must diminish as we travel from the cryohydrate in the direction of the arrows, otherwise there would be two temperatures at which there is the same solubility (*a*, fig. 3, dotted lines) for every solubility between certain limits ; or (*b*, fig. 3, dotted lines) there would be two solubilities for every temperature between certain limits. If we concede the

Fig. 3.
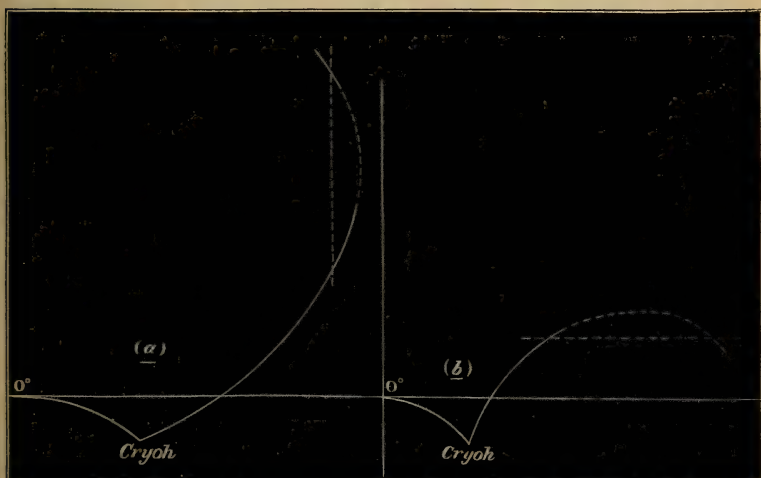
impossibility of these conditions, there appear to be three alternatives—the curve loses curvature either parabolically or hyperbolically, or there must be contrariflexure. The first would carry the conditions into the region of critical state and decomposition. The second might mean, in the case of *a* type, if such asymptote be also parallel to the ordinates, that a certain per cent. ratio of salt is soluble in water at a certain temperature, and at all higher temperatures; in the case of *b* type, if such asymptote be parallel to the abscissæ, that at a certain temperature a finite mass of water will dissolve an infinite mass of salt.

For the experimental examination of this curious question the salt-alloy of nitrate of lead and nitrate of potash, described in § 215, is excellently well adapted. Its composition is 46·86 nitrate of lead + 53·14 nitrate of potash, and its fusing-point, being 207°, is well within the range of the mercurial thermometer. Its constituents at this temperature are far below their temperature of decomposition, and, what is of equal importance, both the nitrates are essentially anhydrous at all temperatures above 0° C.

§ 250. *a* grams of this salt-alloy, finely powdered and freed from condensed moisture, were introduced into a weighed tube. A little water being then introduced through a capillary tube, the end was sealed off, and both reweighed, the amount of water introduced being thus known. The sealed tube was wrapped round in two places with copper wire, and placed in a copper oil-bath. The bath was heated till complete fusion was effected, the water and salt completely mixing to a colourless limpid liquid. The wire enables the tube to be taken out and the contents moved to and fro.

When complete fusion is obtained the bath is allowed to cool slowly, being kept well stirred. The temperature of incipient solidification is observed several times, to avoid possible errors arising from supersaturation, although with this salt-alloy no such condition appears to obtain. As considerable pressure may be exerted on the tube, it and the thermometer were viewed through two sheets of glass six inches apart. None of the tubes, however have burst.

The following results were obtained:—

Percentage of Salt.	Solidifying temperature.
100	207°
99·82	203° or 204°
98·24	197°

§ 251. These results are striking and important. The phenomenon of fusion *per se* is continuous with, and nothing more than an extreme case of, liquefaction by solution. When we are considering such a case as the second, near the top, where 0·18 weight of water dissolve 99·82 of salt, we are induced to regard it as a solution of water in the fused salt rather than the converse, especially as the solidifying-point is so near that of the dry salt. It will be readily granted that a proportion of the alloy and water having even less water than the above will have an incipient solidifying temperature even closer to the temperature of fusion of the dry alloy. Hence

the question, Is this a case of fusion or solution? is to be answered by the reply, It is continuous with both.

The above results with this salt-alloy gave encouragement for the examination of nitre alone with water. The thermal relationship of nitre and water from $-3°$ C., the melting-point of the cryohydrate, to the boiling-point of a saturated solution at one atmospheric pressure, about 115° C., has been pretty fully examined by others and myself. The results are shown in Table LVI. The first sixteen are from my memoir IV., § 129; the next five are on the authority of Gay-Lussac; the last seven, which are those to which I wish here to direct particular attention, are obtained by the use of sealed tubes as described in § 240. The result corresponding to T = 115° is interpolated for the sake of verification from Table LVII. § 253, where a different method of experimenting was undertaken for a different purpose. For T = 100° C., the solution saturated at 114° C. was allowed to cool for several hours in a tube surrounded by boiling water (16·05 grams gave 11·485 grams nitre). For T = 109° C., the solution saturated at 114° C. was allowed to cool for several hours in a tube surrounded by a boiling saturated solution of chloride of sodium (17·83 grams of the solution gave 13·2945 grams of nitre).

§ 252. It must not be overlooked that, although the tubes in the last seven experiments were filled as full of the nitre as the exigencies of manipulation permitted, a certain air-space was unavoidably left into which the water in the tube was free to evaporate. In the last one, indeed, in which water was present its actual weight was only 0·114 gram. This, heated by itself in the free space to 300° C., would have become dry superheated steam. But the fact that it lowered the temperature of solidification 20° C. shows that in the presence of nitre it is not all free. The vapour-tensions of strong solutions of nitre will have to be determined. Correlation with this table or with Wüllner's results is all the more necessary, because, as has been shown by Sorby and others, variation in pressure is not without influence on solubility as well as upon fusion, *per se.*

TABLE LVI.

I.	II.	III.	
A solution of nitre in water containing the following percentage of nitre,	that is, to 1 weight of water containing the following weights of nitre,	begins to solidify at the following temperature C.,	giving up as a solid the following :—
0	0·0000	0 0	Ice.
1	0·0101	−0·1	,,
2	0·0203	−0 3	,,
3	0·0309	−0·7	,,
4	0·0417	−1·1	,,
5	0·0526	−1·5	,,
7	0·0753	−2·2	,,
8·5	0·0929	−2·6	,,
10	0·1111	−2·9	,,
11·2	0·1261	−3·0	Cryohydrate.
12	0·1364	0·0	Nitre.
13	0·1481	+2·0	,,
15	0·1765	+6·0	,,
20	0·2500	+14·0	,,
25	0·3333	+21·0	,,
35	0·5385	+35·0	,,
40	0·6667	+41·0	,,
*43·3	0·7637	+45·1	,,
*49·2	0·9685	+54·7	,,
*55·4	1·2421	+65·4	,,
*62·5	1·6667	+79·7	,,
*70 3	2·3663	+97·6	,,
71·56	2·5162	+100·0	,,
74·56	2·9308	+109·0	,,
74·97	2·9956	+114·0	,,
75·2	3·0323	+115·0	,,
79·14	3·7939	+123·0	,,
84·67	5·5231	+151·0	,,
89·94	8·9404	+201·0	,,
95·11	19·4499	+262·0	,,
98·86	86·7193	+300·0	,,
100·00	∞	+320·0	,,

* Gay-Lussac.

The graphic representation of this relationship is shown in fig. 4, curve A, an ordinate of 1° C. being taken equal to an abscissa of 1 per cent. of nitre. The curve, after dipping to the cryohydrate, rises through 0° C. and reaches the 100 per cent. at 320° C. Perhaps curve B shows the relationship better. It is traced from columns II. and III. It is asymptotic to the temperature-line 320° C., and shows how fused nitre and fused ice are miscible with one another in all proportions.

Fig. 4.
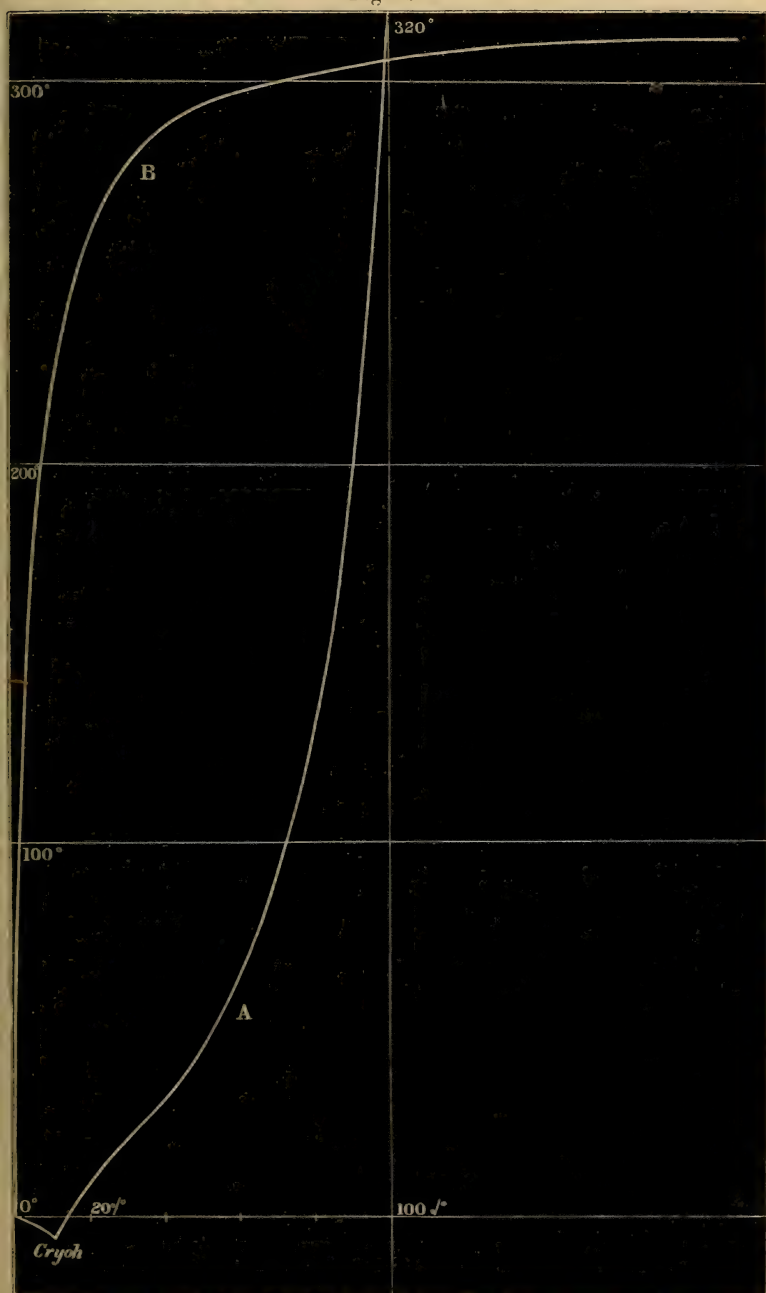
§ 253. *Boiling-Points of Solutions of Nitre.*—To determine the boiling-points of solutions of nitre of various strengths, 40 grams, which were in the later experiments made up to 100 grams, were placed in a clean tin vessel having a narrow neck, together with a thermometer and an indefinite amount of water. The whole was supported in a hot-air chamber so that the neck only of the tin vessel projected. An arrangement was also made for blowing hot air through the upper part of the vessel. By this arrangement it was hoped that the amount of water condensed in the vessel above the liquid would be inconsiderable. The liquid was boiled until a certain temperature was reached. The vessel was then removed, partially cooled, and weighed. This was done at every half-degree. In the table the temperatures are deduced at which boiling occurs in strengths rising 5 per cent. from 20 per cent. In column II. the results are smoothed out under the assumption that there is a rise of 1°·211 for every 5 per cent.

TABLE LVII.

Per cent.	I.	II.
20	101·50	101·50
25	102·83	102·72
30	103·41	103·93
35	104·02	105·14
40	104·50	106·35
45	106·56	107·56
50	107·22	108·77
55	108·85	109·98
60	110·16	111·19
65	110·81	112·40
70	113·00	113·51
75	114·92	114·92

The last of them is saturated at ·758 millim. atmospheric pressure, and the result is inserted in the table, § 252.

§ 254. When a conception such as the above is once fairly grasped, numerous exemplary phenomena which have hitherto been vaguely entertained re-present themselves and claim kindred with it. Thus it is well known that the temperatures of fusion of many organic solids are notably lowered when in contact with water, or even when imperfectly dried ; and this is more marked with those whose temperatures of fusion are not high, and which are nominally classed among insoluble bodies. Such bodies will, especially when in a state of fine division, condense water from the air, and hold it with such

tenacity that they will not relinquish it wholly and imme-
diately when heated to or even above 100° C. Again, acetate
of potassium in solution and subjected to heat, shows continuity
of the liquid condition between strong solution and anhydrous
fusion. Further, if nitrate of ammonium be dried before a
brisk fire, or *in vacuo* over sulphuric acid, it has no associated
water. But a solution of that salt in water passes, on
evaporation over the flame, from the state of solution to that
of fusion without intermediate solidification. Nay, under such
treatment it may begin to decompose before it has become
anhydrous. This has, indeed, led some experimeters to
conclude that in the dry crystalline state it contains a mole-
cule of water. This has arisen from the two facts—first, that
it is hygroscopic in moist air, and, second, that one of the
products of its decomposition in the dry state is water. The
lowering of the boiling-point of a liquid by admixture with
even a very little of another liquid having even a higher
boiling-point is a phenomenon of the same order.

§ 255. *Geological bearing of* §§ 249–254.—Just as in the
selective formation of what in my last memoir were described
as salt-alloys we may have the artificial type of the genesis of
many primary rocks and metamorphic modifications, so in the
wonderful solubility in or miscibility with water of such
alloys and of some salts at high temperatures we may have a
no less clear type of the formation of certain volcanic rocks
and an explanation of some of their peculiarities. The
function of water in affecting rocks has been subjected to
a most exhaustive examination by Daubrée. Water, in
both its solid and liquid form, is a rock. Under pressure
the limit of temperature is not known to which it may be
heated without decomposition, when in contact with bodies
saturated with oxygen. Granting that water may have a so-
called critical temperature, and range above it when it is
heated with bodies which have no physical relationship to-
wards it, still at high pressures it will be compressible as a
vapour to a density at least as great as that of liquid water ;
and until actual decomposition ensues the physical relation-
ship of the water-molecule with the rock-molecule will
remain possibly unchanged. It is true that at the very highest
temperatures water appeared to be decomposed ; but this is
only when it is unconfined.

Whether the earth's temperature be vastly greater towards
its centre than it is near the surface, or whether the observed
increase with depth be confined to a mere skin of the earth,
there seems to be no reason to suppose that water may not,
and does not, exist at the earth's very centre.

If the earth were a sphere of liquid having a density of 5, the pressure at its centre would be over three million atmospheres—a pressure competent to preserve the density of water at a temperature sufficient to fuse perhaps the most refractory known rocks. But at this high temperature the water would, judging by analogy, mix freely with the rock and relieve itself—one cannot yet say how much (compare, however, my next memoir, IX.), but certainly very greatly from its tension.

That there are true sedimentary formations of course no one can deny; but to attribute to marine influence the formation of rocks because water is found within them, or because water is liberated when melted rock-masses are ejected, is a contention no longer supportable. Obsidian melted and under pressure will, I presume, mix freely with water. When this pressure is gradually removed, water-vapour escapes, and although it takes with it a large amount of heat, the temperature of the obsidian may still remain above its point of anhydrous fusion, or it may be maintained fused by heat from other sources. Finally cooled, it is the familiar glassy amorphous mineral. A quick release of pressure entails a quick vaporization of water and a quick loss of heat. The obsidian mass, during and because of the loss of water and the loss of heat, becomes pasty and " rises " like dough during fermentation, and becomes pumice, which is often found overlying obsidian. A quicker release of pressure from above causes the vesicular and vesiculating masses to be projected, and if the vesiculation is carried far and fast volcanic dust is produced. That water is one of the accompaniments of volcanic activity is well known. The presence of hydrochloric acid in the ejecta, and the almost universal neighbourhood of the sea to active volcanoes, has favoured the view that the material for the motive power is supplied by the marine irruption. Without entering upon the question as to whether sea-water is essential to volcanoes, and whether hydrochloric acid is a product of the action of acid silicates or silicic acid upon the chlorides in that liquid, I contend that the evidence is conclusive that at one period the melting masses contain water. They are in the same predicament as the nitre liquified along with water at a high temperature and under corresponding great pressure.

This subject has been so fully discussed by Daubrée in his various memoirs, and is so ably treated in his *Géologie Expérimentale*, that, as far as their geological bearing is concerned, my experiments may be considered as merely adding another chapter to his work.

Graham has shown how alumina, silica, oxide of tin, and oxide of iron may be obtained in aqueous solution in the colloidal state; and Daubrée has proved that at high temperature and under pressure water disintegrates and decomposes certain rocks, and rearranges their constituents, and has argued that, assisted by capillarity and high temperature, many phenomena of volcanism and metamorphism are to be attributed to that agent. He has thus vastly extended the scope of the long-known action of water on silicates, and showed that under conditions of temperature water alone plays as potent a part in such disintegration as the fixed alkalies were known to do under like conditions. My experiments may perhaps be considered as leading us a step further. For they show that water at a high temperature may not only play the part of a solvent in the ordinary restricted sense, but that there is in many cases no limit to its solvent faculty; in other words, that it may be miscible with certain rocks in all proportions : that solution and mixture are continuous with one another. And this continuity, as my experiments prove, is established in some cases,—and these indeed with bodies having no chemical affinity with water,—at temperatures not above the temperatures of fusion of those bodies *per se.* This induces me to think that the replenishment of water in rocks by capillarity, an action upon which Daubrée lays great stress and with regard to which he adduces many striking experiments, is not an essential condition. I must, however, leave the discussion of this question to petrologists.

[NOTE *added June* 16, 1884.—Since the above was in print I have been favoured with a copy of a most interesting memoir by Prof. Tilden and Mr. W. A. Shenstone on the "Solubility of Salts in Water at High Temperatures," read before the Royal Society of London, June 21, 1883 (Transactions of the Royal Society, Part I. 1884). Accordingly, wherever in the two memoirs there may be found similarity in results or ideas, the priority is theirs.

These gentlemen have apparently been to a considerable extent guided by the conception that there is a relationship between the solubility of a salt in water and its temperature of fusion. And perhaps their main argument concerns this relationship. They have made a special study of those interesting cases in which the solid salt contains water of crystallization. This branch of the inquiry I have rather deliberately avoided, as I wished to establish the analogy between metallic and dry-salt alloyage, on the one hand, and water-salt alloyage on the other. Nevertheless they examined the solubility of

nitre in water at 125°.   Their experiments on solubility appear
to stop short far below the temperature of fusion of the salt
per se (excepting in cases where the salt contains water of
crystallization).   They distinctly state, however, that infinite
solubility is " nearly true of benzoic acid, which melts at
120°. . . . . . By sealing it up with water in a glass tube and
heating to a few degrees beyond the melting-point, intermix-
ture occurs in all proportions ; and the liquid so obtained, on
cooling to 120°, or about 1° lower, becomes turbid from depo-
sition of oily drops, which, however, immediately crystallize."
—F. G.]

XIII. *On the Apparent Viscosity of Ice. By* G. S. Turpin *and*
A. W. Warrington, *B.Sc., Students in the Owens College,
Manchester**.

SOME years ago Mr. J. T. Bottomley† devised an experi-
ment to illustrate the effect of pressure on a melting
block of ice.   A stout copper wire with heavy weights attached
at its two ends is slung across a block of ice which is sup-
ported in any convenient manner.   The wire gradually makes
its way through the block ; but the ice constantly re-forms
behind the wire, so that after the block has been cut right
through it is still whole and entire.   The path travelled over
by the wire does not, however, possess its original structure,
but is now semi-transparent, and the block splits readily along
this path.

Bottomley found that string, under the same circumstances
as the copper wire, would not cut through ice.   The explana-
tion he gives is that " the string is not a good enough con-
ductor to relieve itself of the cold in front and pass it back to
the water behind."   In this shape the explanation does not
seem very clear, but in the following expanded form it is
evident enough.   When the wire starts its journey, its upper
surface is in contact with ice-cold water, and its lower surface
in contact with ice.   The pressure of the wire tends to make
the ice beneath it melt ; but before this can occur the latent
heat of liquefaction must be supplied, and in the case of the
copper wire is readily obtained from the water above, which
is in consequence frozen.   The newly formed water is forced
upwards round the wire ; and the same process is repeated
until the wire has made its way through the block.   When,

however, string is used instead of copper wire, this conduction of heat does not readily occur.

In repeating this experiment, water could be distinctly seen moving quickly round the sides of the wire from its under to its upper surface ; and in one particular case, when a brass wire one tenth of an inch in diameter was used with two weights of 56 lb. each, crystals of ice were seen actually growing in the water on the upper surface of the wire, just before it became completely buried in the ice.

In order to determine the effect of conductivity an experiment was made with five different wires. As a matter of convenience, each wire was placed on a separate block of ice, but the blocks were sawn to as nearly as possible the same size. The times taken by the different wires in cutting through the blocks were:—

Wire.	Time, in minutes.	Conductivity.
Silver	192	100
Copper	184	73·6
Brass	267	23·6
Iron	300	11·9
German-silver ...	314	6·3

Each wire was ·67 millim. diameter, and carried $2\frac{1}{2}$ lb. The numbers obtained show that the time taken increases as the conductivity decreases; but there is an apparent exception in the case of the silver and copper wires. To find whether this was due to any difference in the blocks of ice, they were interchanged, with the following result:—

Wire.	Time, in minutes.	Conductivity.
Silver	103	100
Copper	110	73·6

In this case the silver has the advantage ; and the difference in the times, in proportion to the total time taken, is greater than before.

Another experiment was made with the same two wires on one block, each wire being weighted with 20 lb. Results :—

Wire.	Time, in minutes.	Conductivity.
Silver...............	$13\frac{1}{4}$	100
Copper	$15\frac{1}{2}$	73·6

The difference is here one eighth of the whole time, and is again in favour of the silver wire.

These results prove that the time increases as the conductivity decreases; but we have been unable to find any simple relation connecting them together.

Another experiment was made to determine the influence of the weight used. Three pieces of iron wire, cut from the same sample, were loaded with different weights and placed across a block of ice. The times taken in cutting through were as follows:—

Load.	Time, in minutes.	Load × Time.
5 lb.	225	1125
$7\frac{1}{2}$ lb.	$146\frac{1}{2}$	1099
$12\frac{1}{2}$ lb.	84	1090

The numbers in the third column show that the time taken is approximately inversely proportional to the load.

Amongst the experiments made by Pfaff[*] to prove the plasticity of ice is the following one:—An iron tube placed upright on a block of ice is completely surrounded with snow to prevent its temperature rising above 0° C., and a pressure of about two atmospheres is applied at its upper end by means of a one-armed lever: the tube slowly forced its way into the ice, and after an hour had sunk 3 centim. At the close of the experiment Pfaff found inside the iron tube a cylinder of ice, which fitted so closely that it would not fall out by its own weight. From this Pfaff concludes that the sinking of the iron tube is due almost entirely to the plasticity of ice, and only minutely, if at all, to the effect of pressure in lowering the freezing-point of water.

It is, however, at once evident that the explanation given of Bottomley's experiment also applies to this; the only difference being that, whereas in the former case the heat necessary for the liquefaction of the ice under presure is obtained from

[*] Pogg. *Ann.* clv. p. 169 (1875).

the water above the wire, in this it is obtained from the water which is about the sides of the tube. The existence of the tightly fitting cylinder of ice inside the tube, so far from being an objection to this explanation, is a necessary consequence of it.

In order to confirm this explanation, Pfaff's experiment was repeated with four pieces of tubing—of glass, copper, brass, and lead, each about 1 foot long and $\frac{3}{8}$ inch bore. The distances to which the tubes penetrated in four hours are contained in the following table:—

Tube.	Load.	Distance.
Copper	2 lb.	100 millim.
Brass	2 ,,	35 ,,
Lead	2 ,,	7 ,,
Glass	$2\frac{1}{2}$,,	3 ,,

The glass tube was loaded with an extra half-pound in order to make up for its smaller weight.

This shows conclusively that when the experiment is made at a temperature not lower than 0° C., the chief factor is the lowering of the freezing-point by pressure, and not the plasticity of ice. But in the same paper Pfaff describes experiments conducted at temperatures below zero in which the iron tube still penetrated into the ice, though to a very much smaller distance than before. Thus, at a temperature varying from −4° to −1°, the same tube which at 0° sank 30 millim. in one hour, sank only $1\frac{1}{4}$ millim. in twelve hours. In this case the experiment seems capable of explanation only by admitting the presence of a certain degree of plasticity in ice, which is rendered very probable by other experiments described by Pfaff, where a sheet of ice bends gradually under its own weight.

XIV. *On the Thermal Relationship between Water and certain Salts. By* B. Illingworth *and* A. Howard[*].

THE study of the relationship towards water of certain organic salts belonging to one and the same series promised to throw light upon the general question of the relationship between salts and water, inasmuch as the *degree* of difference between the members compared may be made at will very

considerable ; while the *kind* of difference is not to be compared with that resulting from the substitution of an acid or basic element in a given salt.

We have accordingly submitted to examination the sulphomethylate, the sulphoethylate, and the sulphoamylate of potassium (K, $CH_3 SO_4$; K, $C_2 H_5 SO_4$; and K, $C_5 H_{11} SO_4$); and we venture to think that the results are of sufficient interest for us to give the following brief account of them.

We satisfied ourselves that the substances were nearly pure. The methyl salt contained, however, a trace of chlorine, and the amyl salt was not quite free from the same impurity. They were finely powdered, and dried over sulphuric acid in partial vacuum until they ceased to lose weight. A thermometer, the error of which at 0^c was determined, and which was graduated to tenths of a degree (each tenth being $\frac{8}{10}$ millim. long), enabled us to read temperatures with considerable precision.

Sulphoethylate of Potassium (K, $C_2 H_5 SO_4$).—Starting with the ethyl salt, a preliminary examination, made by mixing the salt with about twice its weight of finely crushed ice, showed the cryogen value to be $-13^\circ \cdot 9$ C. This, according to analogy, should be the melting- and solidifying-temperature of the cryohydrate. Solutions containing various percentages of the anhydrous salt were made and submitted to a salt-ice cryogen, the temperature being noted at which solidification began.

With regard to the solubility at the air-temperature :—A solution saturated at 21° C. was allowed to cool for several hours until it reached 15°·1 C. Of this solution, 7·3342 grams were weighed in a covered basin and then dried *in vacuo* over sulphuric acid. The nearly dry mass was powdered and redried until it ceased to lose weight. 4·5732 grams, or 62·35 per cent., were thus obtained.

A solution saturated at the air-temperature was fairly buried in melting ice for several hours and until its temperature had remained for a few hours at 0° C. Examined as above, 24·0880 grams gave 12·9375 grams of anhydrous salt, or 53·71 per cent.

A solution of strength between 40 and 50 per cent. was cooled in an ice-salt cryogen until its temperature remained constant at $-14^\circ \cdot 2$ C. After a considerable amount had solidified, 11·9813 grams of the solution were dried, and yielded 5·3932 grams dry salt, or 45·01 per cent. It will be noted that the temperature of the cryogen of this salt was found to be $-13^\circ \cdot 9$, or $0^\circ \cdot 3$ higher than the melting-point of the cryohydrate.

TABLE of Sulphoethylate of Potassium and Water.

Sulphoethylate of potassium, per cent.	Water. per cent.	Temperature at which solidification begins.	Body separated.
10	90	− 2·2	Ice.
20	80	− 4·9	,,
30	70	− 8·2	,,
40	60	−12·1	,,
45·01	54·99	−14·2 (cryogen −13°·9)	Cryohydrate.
50	50	− 6 (interpolated)	Salt.
53·71	46·29	0	,,
62·35	37·65	+15	,,

Sulphomethylate of Potassium $(K, CH_3 SO_4)$.—The mode of procedure was precisely like that above described.

As a cryogen, it showed a temperature of −11°·3.

At the air-temperature (12°·3) an amount of 5·2254 grams gave 2·8654 grams residue, or 54·8 per cent.

16·5250 of the solution saturated at 0° gave 2·8654, or 47·08 per cent.

The solidifying-temperature of the cryohydrate was found to be −11°·8; and 9·4940 grams of it yielded 3·7824, or 39·84 per cent. anhydrous salt.

TABLE of Sulphomethylate of Potassium and Water.

Sulphomethylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins	Body separated.
10	90	− 2·3	Ice.
15	85	− 3·6	,,
20	80	− 5·0	,,
30	70	− 8·0	,,
39·84	60·16	−11·8 (cryogen −11°·3)	Cryohydrate.
40	60	−11·5 (interpolated)	Salt.
47·08	52·92	0·0	,,
54·8	45·2	+12·3	,,

Sulphoamylate of Potassium $(K, C_5 H_{11} SO_4)$.—This salt [*], on being treated in quite a similar manner, gave the following results.

The temperature of the cryogen was found to be −5° C.

At the air-temperature (17°·3), a solution weighing 6·8099 grams gave 4·0494 grams residue, or 59·46 per cent.

The solidifying-temperature of the cryohydrate was found to be −5·4; and 11·958 grams of it gave 2·8737 grams of

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[*] Probably isoamylate.

anhydrous salt, or 24·03 per cent. 15·667 of the solution, saturated at 0°, gave 5·240 of anhydrous salt, or 33·44 per cent.

TABLE of Sulphoamylate of Potassium and Water.

Sulphoamylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	− 1·9	Ice.
20	80	− 4·3	,,
24·03	75·97	− 5·4 (cryogen −5°)	Cryohydrate.
25	75	− 4·8 (interpolated)	Salt.
33·44	66·56	0·0	,,
59·46	40·54	+17·3	,,

The accompanying figure shows the relationship, in respect to water, of these three closely allied salts.   The abscissæ are percentages, the ordinates temperatures.
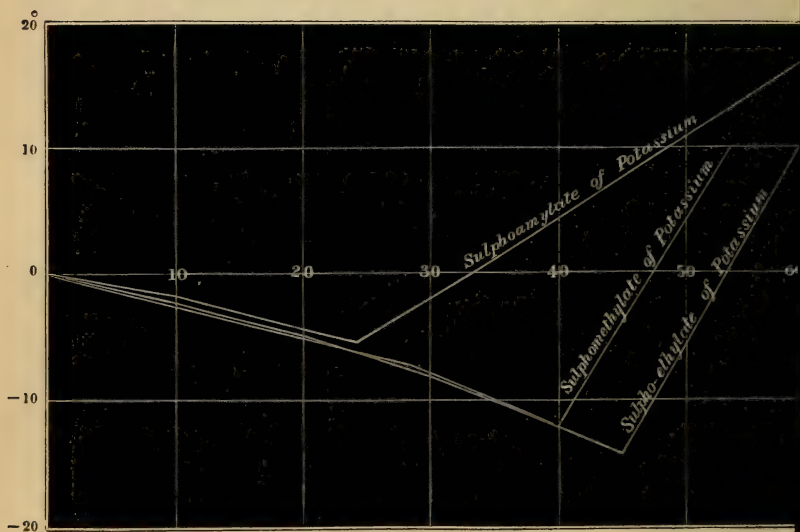
The ethyl and methyl combinations run an almost common course as far as the cryohydrate of the latter.   They cross at about 24 per cent.   The cryohydrate of the ethyl salt contains about 5 per cent. more salt and melts at 2°·4 lower.   The ascending or salt branches of the curves are almost absolutely parallel, but exhibiting a slightly opposite curvature.

Perhaps the most salient fact concerning this group is that the methyl compound is intermediate in these of its physical properties between the ethyl and the amyl members. So interesting did this relationship appear, that we have determined the specific gravities of the three salts. Turpentine was used as the liquid displaced. The dry salt having been weighed in the specific-gravity bottle, a little turpentine was added and the air exhausted. The bottle was subsequently filled with turpentine in the usual way. The air-temperature was $19°·6$, and the specific gravity of the turpentine compared with water at the same temperature was $0·86838$. It was found that

$$\text{at } 19°·6 \begin{cases} \text{sp. grav. of sulphomethylate of potassium} = 2·097, \\ \quad,, \quad,, \quad \text{sulphoethylate of potassium} = 1·843, \\ \quad,, \quad,, \quad \text{sulphoamylate of potassium} = 1·144. \end{cases}$$

Accordingly the densities of the salts are in the inverse order of their molecular weights, and the ethyl compound is in this respect in its usual place between the amyl and methyl relatives.

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  South Kensington.

XV. *Hemihedrism of Cuprite.* By H. A. MIERS, *M.A.*, *Assistant in the Mineral Department, British Museum*[*].

[Plate VI.]

A LOOSE crystal of cuprite (about 4 millim. across), found among a large number of mineral specimens which had been collected by the late Mr. Richard Talling, and which were offered to the British Museum for purchase, was noticed by Mr. Thos. Davies as hemihedral in form.

Subsequently about twelve specimens were found, all from Wheal Phœnix, Cornwall, belonging partly to the same collection and partly to the collection in the Museum, which are characterized by the same peculiarity. This hemihedral development I have been requested by Mr. Fletcher to describe.

It proves to be a mode of hemihedrism of great interest to the crystallographer as one which for more than sixty years has been regarded as theoretically possible, but which has not been hitherto observed on any mineral, and has only recently been proved to exist on artificial sal-ammoniac.

The usual form of the crystals is shown in fig. 4, where a are the cube, o the octahedron, and x the new hemihedral

faces. They vary from the habit of fig. 4, in which the cube predominates, to the similar combination of octahedral habit in which the cube-faces are comparatively small, crystals of cubic habit being most common. The dodecahedron-faces *d* often enter into the combination, as is shown in fig. 5, which represents a third distinct habit characterized by the predominance of the hemihedral form *x*. The only other form observed on these crystals is {2 1 1}. The cube, octahedron, and dodecahedron planes are bright and even, while the faces *x* are bright, but slightly rounded and uneven; they are roughly striated parallel to their intersections with the octahedron, and sometimes parallel to the most remote of the three nearest cube-faces.

The angles, measured and calculated, are as follows :—

Observed.			Calculated.	
Mean.	No. of edges.	Limits.	$x = (986)$.	$x = (875)$.
$(100) : x = 47° \ 30'$	18	$46° \ 39' — 48° \ 22'$	$48° \ 0·7'$	$47° \ 4·7'$
$(010) : x = 53 \ 43$	18	$52 \ 34 — 55 \ 49$	$53 \ 30·8$	$53 \ 25·5$
$(001) : x = 63 \ 58$	18	$62 \ 45 — 64 \ 53$	$63 \ 30·8$	$64 \ 48·6$
$(111) : x = \ 9 \ 23$	11	$8 \ 54 — 10 \ 49$	$9 \ 14·5$	$10 \ 35·6$

The best measurements obtained for a single face *x* to the three cube-faces were 47° 50′, 53° 20′, 64° 4′.

The position of the faces *x* in the figures shows that they afford an example of the hemihedrism which has been described in the text-books of Crystallography * from the time of Mohs as trapezohedral or gyroidal, and as a theoretically possible though hitherto unobserved mode of hemihedrism in the Cubic System. Within the last three years, however, it has been discovered as occurring on one, and has been suggested for another, artificial salt.

If alternate faces of the complete 48-faced figure be suppressed, two half-forms are obtained for which the cubic and dodecahedral planes are no longer planes of symmetry. It was made clear by Mohs † that these two half-forms are enantiomorphous, and may therefore be distinguished as right

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* Groth, *Physikalische Krystallographie*, 1876, p. 221; Mallard, *Traité de Crystallographie*, 1879, i. p. 88 (Hemiédrie holoaxe); Liebisch, *Geometrische Krystallographie*, 1881, p. 246 (γ {h k l}).

† Mohs, *Grundriss der Mineralogie*, i. 1822, p. 170.

and left. With the notation of Miller they may be denoted respectively by $a\{k\ h\ l\}$ and $a\}h\ k\ l\}$.

The faces x are therefore to be assigned to the half-form $a\ \{9\ 8\ 6\}$, though, as may be seen from the limits of variation in the above table, the numerical values of the indices cannot be assigned with absolute precision.

Fig. 1 represents the complete form $\{9\ 8\ 6\}$.

Fig. 2 represents the half-form $a\{9\ 8\ 6\}$, obtained by rejecting the shaded faces, and is the half-form peculiar to cuprite. This is Mohs' left pentagon-icositetrahedron.

Fig. 3 represents the half-form $a\{8\ 9\ 6\}$, obtained by retaining the shaded faces; this is Mohs' right pentagon-icositetrahedron.

It may be noticed that this mode of hemihedrism only affects the form of the 48-faced figure $\{h\ k\ l\}$; so that in the case of cuprite, in which such faces are very rare, it is not surprising that the hemihedral character has hitherto escaped attention. Hexakis-octahedron faces have been figured as occurring holohedrally by W. Phillips [*], and Kokscharow [†], but in neither case have indices been ascribed to the faces.

Where such forms have been noticed upon specimens in the Museum, they are so uneven and irregular that neither their position nor their number can be satisfactorily determined.

The cases in which this trapezohedral hemihedrism has been already recorded are the following :—

(1) Tschermak [‡] observed small faces of $a\{7\ 8\ 5\}$ on artificial crystals of sal-ammoniac, upon edges of the form $p=\{2\ 1\ 1\}$.

Observed.	Calculated.	
	$p=(785)$	$p=(896)$
$p:(121)=13\overset{\circ}{\ }10'$	$=13\overset{\circ}{\ }19{\cdot}7'$	$=13\overset{\circ}{\ }49{\cdot}3'$
$p:(211)=21$	$=20\ 13{\cdot}8$	$=19\ 49{\cdot}8$

It is thus possible that the hemihedral faces of sal-ammoniac and of cuprite may belong to the same form ; but it is remarkable that the crystals of sal-ammoniac exhibit the right, and those of cuprite the left half-form.

(2) Ben-Saude [§] obtained by corrosion with water upon artificial crystals of mixed potassium and sodium chlorides faces which were obliquely striated in such a way as to suggest the presence of small asymmetric faces.

These crystals also exhibited " double refraction in sectors."

Lastly, it has been a question of interest whether this mode

[*] Transactions of the Geological Society, vol. i. 1811, p. 37.
[†] *Materialen zur Mineralogie Russlands*, i. 1853, p. 84.
[‡] *Min. und Petr. Mitth.* 1881, p. 531.
[§] *Bull. Soc. Min. de France*, 1883, p. 260.

of hemihedrism, if observed, would be accompanied by circular polarization *. The crystals of sal-ammoniac did not show it. In the case of cuprite, although many crystals transmit light in irregular patches between crossed Nicols, there is no evidence of circular polarization.

Note.—The cleavage of cuprite is stated in the text-books to be octahedral. The specimens examined on the present occasion show, in addition to the uneven and interrupted octahedral cleavage, a bright and perfect cleavage parallel to the faces of the cube.

XVI. *On the Colour of Chemical Compounds, chiefly as a Function of the Atomic Weights of their Constituent Elements.* —Part I. *Inorganic Compounds.* By THOMAS CARNELLEY, *D.Sc. (London), Professor of Chemistry in University College, Dundee*†.

THERE are at least three circumstances which condition the colour of chemical compounds, viz.:—

1. Temperature.

2. The quantity of the electro-negative element present in a binary compound.

3. The atomic weights of the constituent elements of the compound.

Of these, the first two, together with a few other points in this connexion, have been studied in some detail by Delaval‡, Talbot §, Brewster‖, Schönbein¶, Gladstone**, Houston††, Ackroyd‡‡, Petrie§§, Ross‖‖, and Bayley¶¶. Though it is to the third of these circumstances that I wish more particularly to direct attention in the present communication, yet it

* Groth, *Physikalische Krystallographie*, 1876, p. 223; Von Lang, *Lehrbuch der Krystallographie*, 1866, p. 114.

† Communicated by the Author.

‡ "An experimental Enquiry into the Cause of the Permanent Colours of Bodies," Manchester Phil. Soc. Mem. ii. pp. 147–272 (1789).

§ "Chemical Changes in Colour," Phil. Mag. [3] ii. p. 359 (1833).

‖ "Colour of Natural Bodies," Phil. Mag. [3] viii. p. 468 (1836).

¶ "Cause of the Change in Colour which many Substances exhibit under the Action of Heat," Pogg. *Ann.* xlv. p. 263 (1838); "Colour Changes," Erdm. *Prak. Chem.* lxi. p. 193 (1854); "On the Influence of Temperature on the Colour of Substances," *Basel Verhandl.* i. p. 13 (1857).

** "Effect of Heat on the Colour of Salts in Solution," Phil. Mag. [4] xiv. p. 423 (1857); "Colour of Chloride of Copper in different States of Hydration," Chem. Soc. Journ. viii. p. 211 (1856).

†† "Change of Colour produced in certain Chemical Compounds by Heat," Franklin Instit. Journ. lxii. pp. 115–127 (1871).

‡‡ "Metachromatism," Chem. News, xxxiv. p. 76 (1876); Nature, xiii. pp. 298, 385 (1876); "Selective Absorption," Phil. Mag. [5] ii. p. 423 (1876).

§§ "Metachromatism," Nature, xiii. pp. 347, 426 (1876).

‖‖ Chem. News, xxxiv. pp. 108, 132; also 'Pyrology,' p. 114.

¶¶ "Colour Properties and Colour Relations of the Iron-Copper Group," Chem. Soc. Journ. xxxix. p. 362 (1881).

will be well to state briefly the more important results which have been obtained by other investigators in regard to the first and second.

I. *Influence of Temperature.*—As to the influence of temperature on the colour of chemical compounds, it appears, as shown more particularly by Mr. Ackroyd, that many bodies when heated undergo alterations in colour ; these alterations being such that, as the temperature rises, the colour passes through the following chromatic scale:—

Heating.	White or Colourless.	Cooling
	Violet.	
	Indigo.	
	Blue.	
	Green.	
	Yellow.	
	Orange.	
	Red.	
	Brown.	
	Black.	

In other words, nearly all chromatic changes take place in a definite order, viz. the order of the spectrum colours, in such a way that, as the temperature rises, the colour passes more and more towards the red end of the spectrum ; and subsequently, if the temperature be high enough, to brown and black. Most commonly the colour passes directly from white to pale yellow, the violet, indigo, blue, and green stages being omitted. As examples we may take the following:—

	Normal colour.	Colour assumed as the temperature rises.
ZnO	white	yellow and then orange.
HgI_2, 16° C.	red	dark red.
„ 140° C.	yellow (in sealed tube)	orange and then red.
PbO	yellow	orange and then red.
TlI	yellow	orange-yellow and then orange-red.
$Cu(BO_2)_2$...	blue	green and then greenish-yellow.
$PbCrO_4$ ...	orange	brick-red and then black-red.
AgI	yellowish-white	orange, then red, and finally dark red.
HgO	orange-yellow	orange, then red, and finally brown.

II. *Influence of the Quantity of the Electronegative Element in Binary Compounds.*—It has been pointed out by Ackroyd and by Petrie that, in the case of binary compounds, an

increase in the quantity of the electronegative element produces a colour-change towards the red end of the spectrum, in accordance with the above chromatic scale, for example:—

$Bi_2 O_3$,	yellow.	$Bi_2 O_5$,	brown.
$Sb_2 O_3$,	white.	$Sb_2 O_5$,	yellow.
$Cr_2 Cl_4$,	white.	$Cr_2 Cl_6$,	violet.
$PtCl_2$,	olive.	$PtCl_4$,	orange.
$Cu_2 O$,	red.	CuO,	black.
NiO,	green.	$Ni_2 O_3$,	black.
$Au_2 O$,	green.	$Au_2 O_3$,	brown.
HgI,	green.	$Hg I_2$,	red.
$Cr_2 O_3$,	green.	CrO_3,	red.
FeO,	yellowish.	$Fe_2 O_3$,	red.
PbO,	yellow.	$Pb_3 O_4$, red; PbO_2, brown.
MnO,	green.	$\{$ $Mn_3 O_4$, red-brown; $Mn_2 O_3$, brown-black; MnO_2, black.

We have also a well-known case of this in the colour-changes which the green colouring-matter of plants undergoes during autumn; this green colouring-matter, as oxidation proceeds, passing through the colours green, yellow, orange, brown, dark brown.

III. *Influence of Atomic Weight.*—The influence of atomic weight on the colour of compounds may be stated thus :—In any series of compounds $A_x R_y$, $B_x R_y$, $C_x R_y$, &c., in which R is any element or group of elements, whilst A, B, C, &c. are elements belonging to the same subgroup of Mendeljeff's Table of the Natural Classification of the Elements, given below, the colour passes either wholly or partially through the series:—

	White or Colourless.
	Violet.
	Indigo.
With increase of the Atomic Weight of the elements A, B, C, &c.	Blue.
	Green.
	Yellow.
	Orange.
	Red.
	Brown.
	Black.

Or, in other words, as the atomic weight of the elements A B, C, &c. increases, the more does the colour of the compound pass towards the red end of the spectrum, and thence (in many cases) to brown and black.

The following Table of the Classification is given for comparison, elements belonging to even series being printed in ordinary type and those belonging to odd series in thick type.

TABLE of the Natural Classification of the Elements. (After Mendeljeff)

Groups →	I	II	III	IV	V	VI	VII	Group VIII
Series ↓	Monads.	Dyads.	Triads.	Tetrads.	Triads or Pentads.	Dyads or Hexads.	Monads or Heptads.	
1.	$H=1$							
2.	$Li=7$	$Be=9$	$B=11$	$C=12$	$N=14$	$O=16$	$F=19$	
3.	$Na=23$	$Mg=24$	$Al=27$	$Si=28$	$P=31$	$S=32$	$Cl=35.5$	
4.	$K=39$	$Ca=40$	$Sc=44$	$Ti=48$	$V=51$	$Cr=53$	$Mn=55$	$Fe=56,\ Co=59,\ Ni=59$
5.	$Cu=63$	$Zn=65$	$Ga=69$	....	$As=75$	$Se=79$	$Br=80$	—, —, —.
6.	$Rb=85$	$Sr=87$	$Y=89$	$Zr=90$	$Nb=94$	$Mo=96$	.....	{ $Ru=104,\ Rh=104,\ Pd=106.$
7.	$Ag=108$	$Cd=112$	$In=113$	$Sn=118$	$Sb=120$	$Te=125$	$I=127$	—, —, —.
8.	$Cs=133$	$Ba=137$	$La=139$	$Ce=142$	$Di=147$	.....	.....	
9.	.....	.....	.....	....	$Er=166$	.....	.....	
10.	.....	.....	$Yb=173$	....	$Ta=182$	$W=184$	.....	{ $Os=193,\ Ir=193,\ Pt=195.$
11.	$Au=197$	$Hg=200$	$Tl=204$	$Pb=207$	$Bi=210$	.....	.....	—, —, —.
12.	.....	.....	.....	$Th=234$	.....	$U=240$	.....	—, —, —.

It must be remarked that the above rule applies *only* to those cases in which A, B, C, &c. are elements belonging to the same subgroup, as:—Cl, Br, and I ; Na, Cu, Ag, and Au ; Mg, Zn, Cd, and Hg ; Be, Ca, Sr, and Ba ; Al, Ga, In, and Tl ; O, Cr, Mo, W, and U ; P, As, Sb, and Bi ; &c. ; but not in those cases in which they belong to different subgroups. Thus oxides cannot strictly be compared with the corresponding sulphides, selenides, and tellurides, nor fluorides with the corresponding chlorides, bromides, and iodides, &c. ; for F and O are elements belonging to even series, whereas Cl, Br, I, and S, Se, Te belong to odd series.

The Tables given below will illustrate the colour-relations stated above.

Table of Colour Relations
(showing the influence of atomic weight).

R.	RCl.	RBr.	RI.	R_2S.	R_2Se.	R_2Te.	RF.	R_2O.
Na...	white	white	white $\Big\{$	flesh-coloured	$\Big\}$ red $\Big\{$	dark coppery	$\Big\}$ white	grey
Cu ...	white	grey	cream	black	......	......	red	red
Ag ...	white $\Big\{$	yellow-ish-white	light yellow $\Big\}$	black	black	black	brown	brown
Au $\Big\{$	yellow-ish-white	yellow-ish-grey	golden yellow $\Big\}$	black	......	......	...... $\Big\{$	violet-brown green

R.	R_2SO_4.	R_2SeO_4.	R_2TeO_4.	R_3AsO_3.	R_3AsO_4.	R_3AsS_4.	R_3SbS_4.	R_2CrO_4.
Na...	white	white	white	white	white	yellow	$\Big\{$ pale yellow	$\Big\}$ yellow
Cu ...	......	......	......	......	......	......	......	......
Ag ...	white	white $\Big\{$	dark yellow	$\Big\}$ yellow	red	brown	black	red
Au ...	......	......	......	......	......	......	......	......

R.	RCl_2.	RBr_2.	RI_2.	RS.	RSe.	RTe.	RO.	R_3N_2.
Mg...	white	white	white	white	......	......	white	$\Big\{$ greenish-yellow
Zn ...	white	white	white	white $\Big\{$	lemon-yellow	$\Big\}$ grey $\Big\{$	white, *c.* yellow, *h.*	green
Cd ...	white	white	white	yellow	......	...... $\Big\{$	brown, red when crystalline	...... $\Big\}$
Hg ...	white $\Big\{$	white, *c.* yellow, *h.*	yellow red	red black	steel-grey	$\Big\}$ ...... $\Big\{$	orange-yellow red	dark brown $\Big\}$

R.	$RCrO_4$.	$R_3(AsO_4)_2$.	$R_3(SbS_4)_2$.	$R_2As_2S_7$.	$R(SbO_3)_2$.
Mg...	{ lemon-yellow }	white	white	{ lemon-yellow }	white
Zn ...	yellow	white	orange	{ pale yellow }	yellow
Cd ...	{ orange-yellow }	......	{ light orange }	{ pale yellow }	.....
Hg ..	red	yellow	orange	{ dark yellow }	orange-yellow

R.	RCl_3.	RBr_3.	RI_3.	R_2S_3.	R_2Se_3.	R_2Te_3.	R_2O_3.	RPO_4.	$RAsO_4$.
Al ...	white	white	white	yellow	......	black	white	white	white
Ga .	white	white	white	......	......	......	white	......	......
In ...	white	white	yellow	yellow	......	...	{ pale yellow, *c.* brown, *h.* }	......	......
Tl ...	white	{ pale yellow }	{ yellow, *c.* scarlet, *h.* }	} black	black	...	{ dark reddish brown }	} white	{ lemon-yellow }

R.	RCl_4.	RBr_4.	RI_4.	RS_2.	RSe_2.	RTe_2.	RF_4.	RO_2.
Si ...	white	white	white	white	......	......	white	white
Sn ...	white	white	red {	{ golden-yellow	red-brown	......	...... {	{ white or straw-yellow, *c.* brown, *h.*
Pb ...	......	......	......	(red ?)	......	......	......	brown

R.	RCl_2.	RBr_2.	RI_2.	RS.	RSe.	RTe.	RO.
Si ...	......	......	......	......	......	......	......
Sn ...	white	white	{ yellowish-red	} brown {	{ grey black	} ...... {	{ olive-brown black brown
Pb ...	white	white	{ yellow, *c.* red, *h.* brown, *h, h.*	} black {	{ grey black	} ...... {	{ yellow brown-red

	$RCl_4.$	$RBr_4.$	$RI_4.$	$RO_2.$	$RS_2.$
C ...	white	white	red	white	white
Ti ...	white	{ amber-yellow }	red-brown	white	yellow
Zr ...	white	white	......	white	light brown
Ce ...	......	......	......	{ pale yellow, *c.* red, *h.* }	......
Th ...	white	.. ...	......	white red-brown	yellow black

R.	$RCl_3.$	$RBr_3.$	$RI_3.$	$R_2S_3.$	$R_2Se_3.$	$R_2Te_3.$	$RF_3.$	$R_2O_3.$
P ...	white	white	red	grey-yellow	red	......	white	white
As ...	white	white	light red	yellow	black	......	white	white
Sb ...	white	white	red {	orange black }	black	......	white {	white, *c.* yellow, *h.*
Bi ...	white {	golden-yellow	greyish-black	brownish-black }	black	{ steel-grey }	......	yellow

R.	$RCl_5.$	$RBr_5.$	$RI_5.$	$R_2S_5.$	$R_2Se_5.$	$R_2O_5.$
P ...	white	{ lemon-yellow }	white	grey-yellow	dark red	white
As ...	......	......	white	yellow	......	white
Sb ...	white	......	pale yellow	{ yellow-ish-red }	brown	pale yellow
Bi ...	......	......	brown	......	......	brown

R.	$RCl_3.$	$RBr_3.$	$R_2O_3.$	$RN.$	$R_2O_5.$	$R_2S_5.$
N ...	yellow (?)	dark red	blue	colourless	white	......
V ...	purple	grey-black	black	grey-brown	{ yellow-ish-red }	black
Nb ...	black	......	......	......	white	......
Di ...	rose-red	......	......	......	......	......
Ta ...	......	......	......	{ black-metallic }	white	......

R.	RCl_2	RBr_2.	RI_2.	RS_3.	RSe_3.	RTe_3.	RO_3.
S ...	dark red (?)	red (?)	red (?)	yellow	......	......	white
Se ...	......	......	......	brick-red	red	......	white
Te ...	black	black	black	{ greyish-black }	black	black	{ orange-yellow }

R.	RCl_2.	RBr_2.	RI_2.	RO.	RO_2.	RO_3.	RS_2.	RS_3.
O {	yellow, *g*, orange, *l.* }	......	......	white	......	......	......	......
Cr ...	white	white	......	brown (?)	{ dark brown }	red	......	......
Mo...	yellow	{ yellowish-red }	......	{ black purple-brown }	red-brown violet	white	black	red-brown
W ..	grey	{ blue-black }	green	......	brown	{ yellow, *c.* orange, *h.* }	black	{ black in mass liver in powder }
U ...	......	......	......	......	brown	{ brownish yellow }	black	......

R.	R_2Cl_6.	RCl_4.	RCl_5.	RCl_6.	$RO_2C..$
O	......	......	......	......	......
Cr	purple	......	......	......	red (liq.)
Mo	red	brown	black	......	yellow
W	......	{ greenish brown }	black	dark violet	yellow
U	......	dark green	{ green, reflect. red, trans. }	......	yellow

R.	HgR.	TlR.	CuR_2.	AuR_3.	FeR_2.	Fe_2R_6.	MnR_2.
Cl ...	white	white	liver	reddish	white	red	pale rose
Br {	white	pale yellow	black	black	yellowish	{ dark red }	pale red
I	greenish-yellow	} yellow	......	green	grey	......	......

$R.$	$CoR_2.$	$NiR_2.$	$PdR_2.$	$Ru_2R_6.$	$Ir_2R_6.$	$IrR_4.$	$PtR_2.$	$PtR_4.$
Cl ...	blue	yellow	red {	yellowish brown }	green	red	olive	orange
Br ...	green	golden	......	......	......	......	brown	brown
I	black	black	black	black	black	black	black {	brown-ish-black

In the above tables, elements belonging to even series are printed in ordinary type, and those belonging to odd series in thick type, so that it may be seen at a glance which compounds are comparable with one another. The arrows also show the direction and the extent to which these comparisons may be made.

I have collected in the tables all the available data. The colour attached to each compound is that given in the ordinary text-books, in Watts's Dictionary, and in Gmelin's Handbook. In cases where two different authorities do not agree, I have either given both or have taken the colour of the actual specimen in our college museum. Some compounds, such as HgI_2, HgO, HgS, Sb_2S_3, &c., exist in two differently coloured allotropic modifications*, in which case both colours are entered. In some few instances also there is given in addition to the colour (c) when cold, the next colour (h) which the compound assumes on heating, and sometimes the subsequent colour ($h\,h$) which it assumes when still more strongly heated.

It should not be forgotten that the rule formulated above strictly applies only to compounds in the solid state, and, further, that even in the solid state the colour is liable to vary somewhat with the state of aggregation. In general the colours given in the tables refer to the powdered or precipitated condition.

From the tables it will be seen that out of 426 cases in which the rule may be applied there are but 14 exceptions, viz.: Au_2O, CdO, $TiBr_4$, PBr_5, OCl_2, WCl_4, CrO_2Cl_2, $DiCl_3$, V_2O_5, CrO_3, WI_2, UCl_5, UCl_4, and AuI_3. Of these, two, viz. OCl_2 and CrO_2Cl_2, may be omitted, as the colours given are those of the liquid compounds, whereas the rule, as stated above, is only considered to be applicable to the solid state. According to the rule $TiBr_4$ and PBr_5 should be white, whereas these compounds are generally stated to be pale yellow : it is possible that the *pure* compounds are really white or colourless,

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* Depending no doubt on a difference in the size of the molecule, and in such a way that the modification with a colour nearest the red end of the spectrum will have the largest molecular weight.

and that the pale yellow colour usually ascribed to them is due to the presence of a trace of free bromine or other impurity.

Of the remaining ten exceptions, six (viz. Au_2O, WCl_4, WI_2, UCl_5, UCl_4, and AuI_3) are green instead of being brown or black, and even these will be in accordance with the rule if we accept the modified theoretical explanation given under (*b*), (*vide infrà*). There remain, therefore, only four exceptions (viz. $DiCl_3$, V_2O_5, CrO_3, and CdO) which do not admit of any satisfactory explanation; and even of these CdO is not altogether decisive either one way or another, for though it is brown when in the amorphous state whereas HgO is orange-yellow, yet CdO and HgO are both red when crystalline.

Theoretical Explanation.—For the following theoretical explanation of the phenomena mentioned above, I am chiefly indebted to my friend and colleague Mr. J. W. Capstick, B.Sc.

1. *Influence of Atomic Weight.*—(*a*) In a solid the molecules vibrate as wholes about certain mean positions. Other things being the same (*e.g.* temperature, &c.) the period of vibration will be less as the mass of the molecule is less. If the time of vibration of the molecule is so small as to coincide with some vibration outside the violet end of the spectrum, no visible vibration will be absorbed and the colour of the substance will be white. This state of things must hold until (from chemical substitutions &c.) the mass of the molecule becomes so great as to bring the period of vibration up to the violet end, when the violet rays will begin to be absorbed and the salt will appear of the complementary colour of violet, *i.e.* greenish yellow. If the mass of the molecule be made still greater its period of vibration further increases, and the blue rays begin to be absorbed, and the light left unabsorbed combines to give yellow. Next the green rays are absorbed, and the result is orange. Then the yellow is cut out in addition, leaving only red; and, finally, the red also is cut out, and the substance becomes black.

(*b*) From the colours observed it would appear to be an almost general rule that when the period of vibration becomes great enough to cut out a given colour, it also cuts out all those with smaller wave-length, *e.g.* when yellow is cut out the blue and green are also cut out, otherwise the colours would go from orange to reddish-purple, and then, when the red is cut out (if the blue, green, and yellow were not also cut out), the colour would be greenish instead of the usual black. The green colour of Au_2O, WCl_4, WI_2, UCl_5, UCl_4, and AuI_3 may possibly be accounted for in this way.

2. *Influence of Temperature.*—In the case of a solid the molecules vibrate about certain mean positions, and a rise of

temperature means a greater amplitude of vibration, but not a greater period. In fact, if the vibration be not quite harmonic a greater amplitude may, as in the pendulum, require a longer period. In addition to this a rise of temperature weakens the cohesion between the molecules, and hence lessens the force of restitution, thus causing the molecule to vibrate more slowly, and consequently producing the same changes of colour as are observed when the mass of the molecule is increased. (For Ackroyd's explanation of the colour-changes produced by heat see 'Chemical News,' xxxiv. p. 76.)

The above theory appears to account fully for the otherwise paradoxical fact, that either increase in molecular weight or increase in temperature produces identically the same series of colour-changes.

The phenomenon referred to under II. (viz., that in any binary compound an increase in the quantity of the electro-negative element produces a colour-change towards the red end of the spectrum) is probably due to the increase in the molecular weight caused by the greater quantity of the electro-negative element which the compound contains, and is hence also fully accounted for by the above theory; though, for this explanation to hold good throughout, it would be necessary in some cases, as in those of the oxides of Cu, Pb, and Cr, to double or treble the generally received formula of some of these oxides, thus :—

$Cu_2 O$ (red), $Cu_2 O_2$ (black) ; $Pb_3 O_3$ (yellow), $Pb_3 O_4$ (red), $Pb_3 O_6$ (brown) ; $Cr_2 O_3$ (green), $Cr_2 O_6$ (red).

Finally, there is also some indication of the colour of compounds being a *periodic* function of the atomic weight. This is best seen in the case of the normal iodides. If a curve be constructed in which the ordinates represent the atomic weights of the positive element, and the abscissæ a chromatic scale rising from black through brown, red, orange, yellow, green, &c., to white, then the curve so obtained will be of a nature similar to Lothar Meyer's well-known curve of the elements.

In a subsequent paper I hope to apply the above facts to the colours of organic compounds, whereby I believe it will be possible to trace a connexion between the composition and the colour of many dye-stuffs.

XVII. *Preliminary Notice of a new Sunshine-Recorder.* *By* Herbert M'Leod[*].

BEING somewhat doubtful of the accuracy of the pub-
lished reports of the duration of sunshine, in the
summer of 1880 I tried to devise some apparatus by which
the light, instead of the heat of the sun, would be used to
produce the record of sunshine. Several trials were made;
and in some of them clockwork was employed to move strips
of sensitive paper. The simplest form of apparatus I have
recently tried again, using the ferroprussiate paper now much
employed by engineers for copying tracings, and which is
preferable to silver paper, first, in consequence of its
cheapness, and, secondly, because of the ease with which the
image is fixed, as for this purpose washing in water is
sufficient.

The apparatus consists of a camera so fixed that its axis
is parallel to the polar axis of the earth, the lens pointing
northwards. Opposite the lens a silvered sphere is placed.
The rays from the sun are reflected from the sphere through
the lens of the camera on to the sensitive paper, on which a
distorted image of the sun is formed ; and the positions of the
lens and sphere are so arranged that the image is a linear one
and radial. By the motion of the earth the image is carried
round in a circular arc, tracing a curve on the sensitive
paper. In the instrument at present constructed, the sphere
is a chemical round-bottomed flask silvered inside, and about
95 millim. in diameter ; the distance from flask to lens is
76 millim., and from lens to sensitive paper 152 millim. ; the
lens has a focal length of 90 millim. and an effective
aperture of 22 millim.

The circle traced by the sun in June is about 120 millim.
in diameter. An impression is made on the paper by exposure
for only 10 seconds ; and when the lens is covered for one
minute, a light line is produced in the circular band, so that
the paper is sufficiently sensitive in the present apparatus to
register short gleams of sunshine, and also the passage of
small clouds. When the sun is shining through light clouds,
an impression is produced on the paper, but somewhat
blurred, and of a much less intense blue colour than is
obtained by bright sunshine. The time-scale is made by
drawing from the centre of the circular band radial lines,
containing between them angles of $15°$, each of which
represents one hour of time.

[*] Communicated by the Physical Society. Read June 28, 1884.

It still remains to be found which are the most convenient dimensions for the globe and lens, so that the minimum of alteration of position will be requisite to obtain a sharp image during all times of the year ; and also the best method of fixing the paper so that it may be easily changed and the time-scale marked on it.

XVIII. *Permanent Magnets.*—I.
By R. H. M. Bosanquet, *St. John's College, Oxford.*

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

IN some notes on this subject (Phil. Mag. xv. pp. 205, 257, 309) I showed that, when a permanent magnet is divided into short lengths, its total moment is considerably diminished. I also endeavoured to treat the theory of the question from what I take to be Faraday's point of view. The measures then executed were only of one element—the moment. The view of the phenomena was therefore insufficient. Having now in my hands processes for determining the magnetic induction in the magnet, I have made determinations of this element, as well as of the moment, in three compound magnets. Further, I have measured in one magnet the number of ampere-turns of a uniformly wound coil necessary to reduce the external action temporarily to zero. These measures form the first part of this communication. I find that the properties of magnets, between the state of thin disks and bars of about five times the length of their diameter, are governed by extremely simple laws. Yet these are of such a nature that I am unable to imagine how the vague generalities about induction, which some consider sufficient to account for the facts I have previously brought forward, can be applied to them with any useful result.

I then show how the theory I have based on Faraday's views offers an account of the phenomena, and especially of the cases comprised within the above limits.

The complete determination of the functions involved in the case of bars of greater length will require additional experiments.

N = total number of pieces into which a whole bar is divided.

Then, if m, n be two numbers such that $mn = N$,

m is the number of separate bars in any combination,
n the number of pieces in each separate bar of the combination,

x is the length of the separate bar,

l　　,,　　,,　　,,　　whole bar,

M, total moment of m bars of n pieces each,

$\dfrac{M}{m}$, moment of one bar of n pieces,

𝕭, magnetic induction (lines of force per unit area, field-intensity) through equatorial section of bar of n pieces,

R radius of bar,　$S = \pi R^2$,

$F = \dfrac{4\pi \text{ moment}}{S\mathfrak{B}} = $ focal distance*,

$f = \dfrac{F}{x} = $ focal distance, length unity.

Bar A.

N $= 18$.　$l = 28\cdot65$ centim.　R $= \cdot978$ centim.

n	1.	2.	3.	6.	9.	18.
M $\{$ Obs.	418	687	928	1773	2372	3494
$\quad\{$ Calc.	418	686	954	1758	2562	4974
Obs.$-$Calc. ..	0	$+1$	-26	$+15$	-190	-1480
$\dfrac{M}{m}$	23·2	76·0	154·7	591·0	1186	3494
𝕭 $\{$ Obs.	38·9	74·5	123·1	275·4	361	594
$\quad\{$ Corr.	46	92	138	276	..	..
f	1·33	1·09	·982	·933	·959	·859
F	2·11	3·45	4·69	8·92	13·7	24·6

$$\left.\begin{array}{l} \text{M calc.} = 150 + n\ 268 \\ \text{𝕭 corr.} = n\ 46 \end{array}\right\} \text{ up to } n = 6.$$

The limiting value of F when $n = 0$ is, according to these expressions, $F_0 = \cdot758$ centim.

$$\frac{F_0}{R} = \cdot775.$$

(As to the calculation of F_0 see *post.* (2).)

The total moment has a finite but small limit ($= 150$), when the bar is supposed to be divided into an infinite number of thin disks. As to the persistence of the linear laws in the case of actual disks of small thickness, see bars B and C *post.* The moment increases with increments proportional to those

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* The points thus defined would be the poles, if the conception of poles were true and applicable; in bars the distance of the foci is usually a little less than that of the poles as ordinarily defined. In the present paper the foci are made use of as indicating by their position the distribution of the magnetism. They may be also regarded, with reserve, as the points of application of the resultants of the lines of force.

of n till after the point where $n=6$, after which the moment falls below the linear value.

Bar A.

Curve of Total Moments. n pieces in each of the m bars into which the whole is divided.
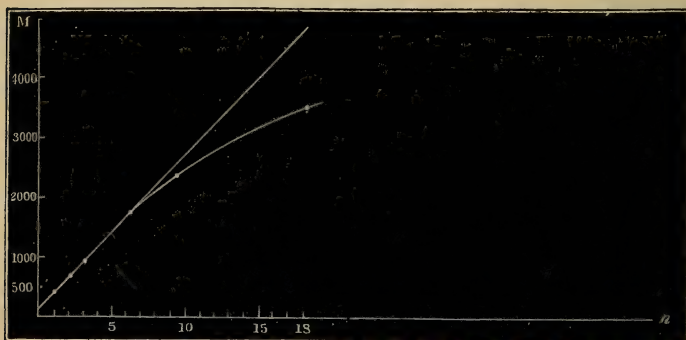
Bar A.

Curve of Induction (intensity), in equatorial section of bar of n pieces.
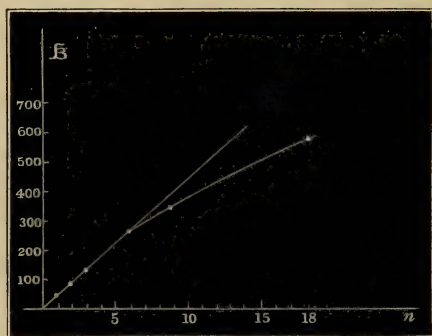
The moments were measured in the bifilar and the torsion-balance. They were originally measured in the bifilar with all the pieces in one tray in each state of combination. The discrepancy then found between the limiting moment and the moment of the current-turns required for temporary demagnetization (see *post.*), gave rise to the suspicion that the induction between the pieces dispersed about the tray was not negligible. The measures were then repeated, the smaller combinations being taken three together. The numbers thus obtained are those above given. The accordance with the temporary demagnetizing force being still imperfect, though

much improved, a set was made with each piece separately. The moments had all fallen, but in proportion ; so that there was no evidence of induction interfering in the values which are given.

The constant of the bifilar was determined by vibrating a leaden rectangle having the same weight as the tray and magnet, and a known moment of inertia. The same suspension-stirrup was used in both cases ; its moment of inertia was determined separately. An approximate value of H was employed.

The constant of the torsion-balance was determined by vibrating a lead rectangle. The variation of the torsion with the weight was inconsiderable in amount with the wire now employed, but was somewhat irregular. It is very difficult to get wire at all suitable for this purpose. Besides the variation of the constant of torsion, most wires take sets in loading and unloading to such an extent as to make them nearly useless. The best wire I have had is excessively hard. By dint of great labour reliable readings were obtained.

The first numbers given for $\mathfrak{B}$, and the figure*, represent the results of experiment. Rowland's method was employed; ten induction-coils for $n=18, 9, 6, 3, 2$, and fifteen for the singles. It is clear, however, and was so from a preliminary set, that these results need correction. For, according to the course of the numbers, the induction would vanish, and then become negative for finite lengths, which is inconceivable.

The source of the error is doubtless in the fact that, with short lengths, the coils cannot be sufficiently concentrated about the equatorial sections. The coils, though bound up closely, extend over a considerable part of the length of the short bars. I have found by direct experiment that spreading the induction-coils leads to considerable diminution of the observed induction. In the present series it was impossible even to fit the 10-coil closely to the bars, as the packing had to pass within the coils. But the coil of 15 was packed so as to fit the singles very closely indeed : the error of the corresponding value was thus reduced to about two thirds of its former amount.

There can be no doubt that the straight line which marks the course of the lower inductions ought to go to the origin, instead of falling just below it (see figure above). Then up to $n=6$ we have $\mathfrak{B} = n\,46$. This assumes that the value for $n=6$ is correct, since the error due to the coil must be by this time small. The strengths of the different short bars varied a

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* As originally drawn. The line in the woodcut passes through the origin instead of a very little below it.

good deal. They were all examined, and an average taken for each type.

In order to ascertain whether the law as to a finite limiting moment held good for further subdivision, two short bars were constructed of thin disks of sheet steel, hardened, ground, and fitted. Of these B had the same diameter as A, C a diameter about twice as large. As these bars were short, $\mathfrak{M}$ could not be accurately ascertained for their subdivisions. But as both were well within the linear range, it is assumed that a law holds similar to that in the case of A. The value of $\mathfrak{M}$ for the whole bar was ascertained by experiment in each case.

Bar B.

N = 20. $l = 3.992$ centim. R = $\cdot$978 centim.

n	1.	2.	4.	5.	10.	20.
M { Obs. .	22·2	27·6	35·5	41·6	66·2	109·4
{ Calc. ..	22·6	27·2	36·4	41·0	64·0	110
Obs.—Calc.	−·4	+·4	−·9	+·6	+2·2	−·6
$\dfrac{M}{m}$	1·11	2·76	7·1	10·4	33·1	109·4
$\mathfrak{M}$ { Obs. ..	..	..	..	..	..	101
{ Calc...	5·05	10·1	20·2	25·2	50·5	
f	4·60	2·86	1·84	1·73	1·37	1·13
F	·919	1·14	1·47	1·73	2·74	4·53 centim.

M calc. $= 18\cdot0 + n\ 4\cdot6.$

$\mathfrak{M}$ calc. $= n\ 5\cdot05.$

The limiting value $F_0 = \cdot745$ centim.

$$\frac{F_0}{R} = \cdot762.$$

Bar C.

N = 18. $l = 3.647$ centim. R = $1\cdot905$ centim.

n	1.	2.	3.	6.	9.	18.
M { Obs. ..	26·3	29·1	32·7	42·0	50·1	82·3
{ Calc. ..	26·0	29·3	32·6	42·5	52·4	82·1
Obs.—Calc...	+·3	−·2	+·1	−·5	−2·3	+·2
$\dfrac{M}{m}$	1·46	3·23	5·45	14·0	25·0	82·3
$\mathfrak{M}$ { Obs. ..	..	..	..	..	..	20·0
{ Calc. ..	1·11	2·22	3·34	6·67	10·0	..
f	7·15	3·96	2·96	1·91	1·51	1·24
F	1·45	1·60	1·80	2·32	2·76	4·54 centim.

$$\text{M calc.} = 22{\cdot}7 + n\,3{\cdot}3.$$
$$\mathfrak{B} \text{ calc.} = n1{\cdot}111.$$

The limiting value $F_0 = 1{\cdot}25$ centim.,

$$\frac{F_0}{R} = {\cdot}657.$$

The expressions above arrived at for bars within the range covered by the linear relations may be put in a more convenient form by introducing x, the length of the cylinder, instead of the number n, into the expressions. Remembering that

$$mn = N, \quad mx = l,$$

and putting

$$M = M_0 + nM',$$

where M_0, M' are constants, the moment of a bar of length x is

$$M_x = \frac{M}{m} = \frac{x}{l}\,M_0 + \frac{x^2}{l^2}\,NM'.$$

Again, putting $\mathfrak{B} = n\mathfrak{B}'$, where $\mathfrak{B}'$ is a constant,

$$\mathfrak{B} = \frac{x}{l}\,N\mathfrak{B}'; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

also

$$f = \frac{4\pi M_x}{x\mathfrak{B}S}$$

$$= \frac{4\pi}{\mathfrak{B}'S}\left(\frac{M_0}{Nx} + \frac{M'}{l}\right),$$

$$F = fx = \frac{4\pi}{\mathfrak{B}'S}\left(\frac{M_0}{N} + \frac{M'}{l}\,x\right).$$

In this last put $x = 0$, then

$$F_0 = \frac{4\pi M_0}{N\mathfrak{B}'S}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

Applying these formulæ, we find for bars of length x, magnetized in the same manner as A, B, C respectively, the following expressions, within the linear range:—

	A.	B.	C.
M_x	$5{\cdot}24\,x + 5{\cdot}88\,x^2,$	$4{\cdot}51\,x + 5{\cdot}77\,x^2,$	$6{\cdot}22\,x + 4{\cdot}46\,x^2.$
$\mathfrak{B}$	$28{\cdot}9\,x,$	$25{\cdot}30\,x,$	$5{\cdot}483\,x.$
f	$\dfrac{{\cdot}758}{x} + {\cdot}851,$	$\dfrac{{\cdot}746}{x} + {\cdot}955,$	$\dfrac{1{\cdot}25}{x} + {\cdot}898.$
F	${\cdot}758 + {\cdot}851\,x,$	${\cdot}746 + {\cdot}955\,x,$	$1{\cdot}25 + {\cdot}898\,x.$
$\dfrac{F_0}{R}$	${\cdot}775,$	${\cdot}762,$	${\cdot}657.$

L 2

The moments of B and C were determined by suspending the combinations in a tray in the torsion-balance.

I have hitherto assumed that the resultant magnetism of a disk, or short cylinder, acts, as it is commonly supposed to do, at the terminal surfaces. It is now clear that the foci, as I define them, are at a distance greater than the length of the short cylinder. This distance tends to a finite limit for thin disks. The limiting focal distance appears to be about three fourths of the radius.

This idea is new to me, though it is an obvious deduction from the general appearance of the lines of force. It will probably also hold for electromagnets.

By the foregoing investigation we have reduced the moment of the magnet to that of a series of infinitely thin disks, which correspond to the magnetic shells of the amperian theory. In the case of bar A, for example, the total moment of the whole magnet is more than twenty times as great as the limiting disk-moment. It now appeared to be of interest to see what would be the number of current-turns which would be required to demagnetize the magnet temporarily. It was to be expected that the moment of the current-turns required would be equal to the limiting disk-moment.

The magnet was enclosed in a coil of 255 turns having exactly its own length, and was placed on the deflection-scale near the needle so that it produced a deflection of about 20°. A current was then sent through the coil, so as to reduce the deflection to zero. The first time this is done, it always reduces the permanent magnetism a little. The value employed must therefore be ascertained before all the other measurements are made.

$$\text{Ampere-turns which demagnetize A } = 430.$$

$$\frac{\text{Ampere-turns } \times \text{ area of magnet}}{10} \quad . = 129.$$

$$\text{Limiting disk-moment of A } . \quad . \quad . = 150.$$

It has been mentioned that the distribution of the magnetism in A was far from uniform. It seems probable that the uniform coil acts with an advantage over the irregular distribution in the magnet. And if this be the case, we must suppose that the actual disk-moment of 150 is balanced by the effect of a uniform coil corresponding to 129. In fact it is known that a difference of potential localized at a point in a bar, as

by a small coil carrying a current, produces a magnetic short circuit through the surrounding medium, instead of contributing in full measure to strengthening the general distribution. However this may be, the broad features are that the total moment of A, amounting to about 3500, is neutralized by the action of a coil which would be measured by 129, or somewhat less than the disk-moment[*]. It is clear that the consideration of moments lends no convenient shape to the problem.

Consider instead the magnet as decomposed into a number of thin disks, each of which can be represented according to the fundamental convention of electromagnetism by a current round its edge. Then the number of current-turns is represented by the quotient of the moment by the area.

$$\text{In magnet A,} \quad \frac{150}{\text{area}} = 49 \cdot 9 \text{ current-turns,}$$
$$= 499 \text{ ampere-turns.}$$

Ampere-turns in demagnetizing coil $= 430$.

Allowing, as above, for the discrepancy, we assume for the present that the demagnetizing current-turns are equivalent to those of the limiting disk-moment.

If, therefore, we conceive of a permanent magnet as having a magnetic potential imbedded in its substance of the same nature as that which would be due to amperian currents, and acting on the steel in the same manner as an external potential produced by a coil, we have a convenient statement of the facts. For the amperian currents, or the potential, have been measured in two ways, viz. by cutting up into disks and by neutralization with a coil; and the results are accordant, allowing for the imperfections and difficulty of the investigation.

I proceed to develop the mode of accounting for the foregoing facts by Faraday's analogy of the voltaic circuit; that is to say, by the application of an analogue of Ohm's law:—

$$\text{Magnetic resistance} = \frac{\text{Diff. of Potential}}{\text{Intensity}}.$$

I formerly called Difference of Potential, Magnetomotive

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[*] The radius of the coil being about 1·27 centim., its total moment was about 218. But it is conceived that the space external to the magnet cannot have exercised any considerable action on the needle, nor any on the magnet.

Force, to emphasize the analogy with electromotive force. Intensity is the same as Magnetic Induction, or lines of force per unit area, and is represented by $\mathfrak{B}$.

We will first consider what I have called the linear range ; that is to say, the case of cylinders whose length does not exceed ten times their radius, including thin disks.

We suppose the steel to have a difference of magnetic potential imbedded in it per unit of length, corresponding to the values observed.

$$\text{Potential per unit length} = \frac{4\pi M_0}{l \times \text{area}} = P',$$

and

$$\text{Potential of length } x \qquad = P'x.$$

Now within the linear range $\mathfrak{B} = B'x$ say, where B' is the coefficient given at (1),

$$\therefore \text{Magnetic resistance} = \frac{P'}{B'},$$

and is constant within the linear range.

Further, by (1) the value of B' is $\dfrac{N\mathfrak{B}'}{l}$;

$$\therefore \text{Magnetic resistance} = \frac{\dfrac{4\pi M_0}{lS}}{\dfrac{N\mathfrak{B}'}{l}} = \frac{4\pi M_0}{N\mathfrak{B}'S},$$

which is the same as the value of F_0 (2).

It is at once apparent that this must be so. For the resistance is the altitude of a cylinder which would have the same resistance as the actual distribution; and in the case of the disk this is the same as the distance between the points of application of the resultants of the lines of force.

Hence the magnetic resistance throughout the linear range is constant: it is nearly three fourths of the radius in A and B, and about two thirds of the radius in C. This is nearly equal to the resistance at one end of an open organ-pipe. If we could arrive at this independently by an extension of reasoning such as that employed in connexion with the open ends of organ-pipes, we could found the whole theory upon it. As it is, the admission of this law throws some light on the laws of the linear range.

For let P' be the potential per unit length, and ρ the

magnetic resistance, then

$$\mathfrak{B} = \frac{\mathrm{P}' x}{\rho};$$

which accounts for $\mathfrak{B}$ being proportional to the length, or to the thickness of the disk, the point which it seems impossible to deal with by the method of induction.

As to the focal distance, or distance between the points of application of the resultants, it is easy to see that for thin disks it must be nearly equal to some constant, which we may call F_0. We can thus establish for the moments of very thin disks the formula

$$\text{Moment} = \frac{\mathfrak{B} \mathrm{S} \mathrm{F}_0}{4\pi} \ (\mathrm{S} = \text{area});$$

and putting for $\mathfrak{B}$ its value,

$$\text{Moment} = \frac{\mathrm{P}' \mathrm{S} \mathrm{F}_0}{4\pi\rho} x;$$

or if a bar of length l be divided into m pieces, so that

$$x = \frac{l}{m},$$

then the moment of one piece . . . . $= \dfrac{\mathrm{P}' \mathrm{S} \mathrm{F}_0}{4\pi\rho} \dfrac{l}{m}$,

and total moment of bar cut up into pieces $= \dfrac{\mathrm{P}' \mathrm{S} \mathrm{F}_0}{4\pi\rho} l$,

a finite limit when m is great.

We cannot deal accurately with the intervening distributions, as they require the knowledge of the value of F in order to obtain the moments from the inductions. But we may consider the case, which is not far from the truth, for bars whose length is about half the limit of the linear range, viz. where we suppose $\mathrm{F} = x$, or $f = 1$, or that the foci are at the ends of the bar. It will be seen that this is very nearly true for $n = 3$ in bar A. In this case, putting x for F,

$$\text{Moment} = \frac{\mathrm{P}' \mathrm{S}}{4\pi\rho} x^2;$$

and for a short range the moment can be expressed approximately in terms of the square of the length. The true forms of the expressions throughout the linear range have been given above.

Then if, as before, a bar of length l be divided into m pieces, so that $x = \dfrac{l}{m}$,

$$\text{Moment of one piece.} \quad = \frac{P'S}{4\pi\rho}\frac{l^2}{m^2},$$

$$\text{Total moment of } m \text{ pieces} = \frac{P'S}{4\pi\rho}\frac{l^2}{m}.$$

Although it would probably not be easy to determine F by independent reasoning of a simple character, it is not difficult to see that it must be the sum of F_0 and some fraction of x such as ·8 or ·9 ; and, admitting this, we obtain the form of the general expression for the moment within the linear range, thus :—

$$\text{Moment} = \frac{\mathfrak{B}SF}{4\pi}$$

$$= \frac{P'S}{4\pi\rho}x(F_0 + \cdot9x) \text{ say,}$$

which fairly represents the actual expressions.

In the region beyond the linear range the magnetic resistance increases; the fall of both moments and inductions below the linear values (see figures to bar A) can be represented as due to this, as is clear from the formula last written down. Some values of the magnetic resistances are subjoined.

Bar A.

Magnetic Resistance of Bar of n pieces.

	n	1, 2, 3, 6.	9.	18.
Calc. { From disk-moment . .		·758	·869	1·056
{ From demagnetization .	. . .	.	.	·909
Induction { pieces in right order	. .	.	. .	·891
under H, 100 coils { reversed in pairs	. .	. .	. .	1·011

By induction produced in demagnetization, 10 coils   ·928

$$\text{Formula for resistance from disk-moment} \quad = \frac{4\pi\,150}{mS\mathfrak{B}},$$

$$\text{,,} \qquad \text{,,} \qquad \text{,,} \qquad \text{demagnetization} \ = \frac{4\pi \times 43}{m\mathfrak{B}}.$$

There is a fair accordance considering the difficulties introduced by the want of uniformity. An endeavour will be made to obtain a magnet in more uniform condition.

The increase of the magnetic resistance with the length of the bar is without doubt to be ascribed to the intrinsic magnetic resistance of the steel.

The discovery of the precise laws of magnetic resistance in such cases must form the subject of further experiment.

The bars B and C so slightly affect an external needle that the demagnetization-experiment cannot be made on them with any accuracy. It is not in any case an experiment of a very accurate character, and perhaps too much stress may be laid on the want of exact accordance between its results and others.

XIX. *Notices respecting New Books.*

The Scientific Papers of JAMES PRESCOTT JOULE. *Published by the Physical Society.* Vol. I. London: Taylor and Francis. 1884.

WE have the authority of the Prime Minister for the statement that the present age is not one abounding in minds of the first order. Perhaps not, from the popular (*i. e.* the superficial) point of view. But that it can hold its own, in this respect, with any previous age, will undoubtedly be the verdict of posterity. For the true and only test of a " mind of the first order " is to be sought in the creations of that mind, and their influence for good upon the intellectual and moral progress of our race. It may be that there is a dearth of popular idols—literary, artistic, political, philosophic, &c. What of that? Alike in the study of the mathematician and in the laboratories of the chemist, the physicist, and the physiologist, are now being developed ideas, results, and processes which will have an influence on the future, in comparison with which the utmost efforts of statecraft are but as a drop in the bucket. Watt and Faraday, Wöhler and Liebig, Lister and Pasteur, Helmholtz and Thomson :—what achievement of statesman or warrior in any age can be compared, either in intellectual grandeur or in true usefulness, with theirs?

> " Regum timendorum in proprios greges,
> Reges in ipsos imperium est Jovis."

The quiet, all but unknown, student is in these latter days the real master of monarchs and of civilization. But such a theme as this is unsuited to a scientific journal, and must be left to the next *Vates sacer*, if such a phenomenon be any longer possible.

The volume before us is the work of a mind undoubtedly " of the first order." As usually happens to a great discoverer, Joule's earlier efforts were received with coldness, even suspicion ; then (as Whewell remarked of Forbes and his Glacier-Theory) they passed to the second stage, in which they were acknowledged to be true, *but not new*. This stage, also, was of short duration, and Joule's transcendent merits are now all but universally recognized.

Not Copernicus and Galilei, when they abolished the Ptolemaic system; not Newton, when he annihilated the Cartesian vortices; not Young and Fresnel, when they exploded the Corpuscular Theory; not Faraday and Clerk-Maxwell, in their splendid victory over *Actio in distans*—more thoroughly shattered a malignant and dangerous heresy, than did Joule when he overthrew the baleful giant Force, and firmly established, by lawful means, the beneficent rule of the rightful monarch, Energy! Then, and not till then, were the marvellous achievements of Sadi Carnot rendered fully available; and Science silently underwent a revolution more swift and more tremendous than ever befel a nation. But this, also, must be a theme for the Poet of the Future!

To be pedantic, if not also prosaic, is the fate (usually self-imposed) of most commentators. We will therefore content ourselves with a brief analysis of the contents of the present volume, while expressing the hope that its successor may soon appear; and we offer, in passing, our cordial thanks to the Physical Society for this great boon to Science.

The present volume is confined to papers by Joule himself; and the happy adoption of the chronological order enables the reader to follow, step by step, the progress of his scientific career. We can trace how, by his early electromagnetic investigations, he was led to study the Voltaic pile; how, in a brief note of 1840 (p. 59), he puts in a few words the whole experimental laws of the production of heat by the resistance to the passage of a current; and how this, in its turn, led him to the heat of electrolysis, and its connexion with heat of combination. Then it is, as it were, quite a natural step to the grand paper "On the Calorific Effects of Magneto-electricity, and on the Mechanical Value of Heat" (1843). This paper contains, in an Appendix, the remarkably close approximation to the true value of the Dynamical Equivalent of Heat which Joule obtained by the friction of water in narrow tubes, and the first hint of the application of his views to animal physiology. It was followed in the succeeding year by another epoch-making paper "On the Changes of Temperature produced by the Rarefaction and Condensation of Air." But it skills not to go through, in this way, what might be obtained from the mere Index:—the book must be read. And the reader who knows only the grander facts for which Joule now gets credit will certainly at intervals pause, and ponder on the strange freaks of even scientific history, when he meets with a well-known fact or theory which, though perhaps it has made the fame of some more recent investigator, is now seen to have been given, long ago, by Joule.

After all, he will probably conclude that "minds of the first order" are still by no means rare. And he will be confirmed in that conclusion by every additional volume which appears, of the collected works of living men like Stokes and Thomson, and of the mighty dead like Henry Smith and Clerk-Maxwell.

XX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xvii. p. 559.]

February 20, 1884.—Prof. T. G. Bonney, D.Sc., F.R.S.,
President, in the Chair.

THE following communications were read :—
1. " On a recent Exposure of the Shelly Patches in the Boulder-clay at Bridlington." By G. W. Lamplugh, Esq.

2. " On the so-called *Spongia paradoxica*, S. Woodward, from the Red and White Chalk of Hunstanton." By Prof. T. McKenny Hughes, M.A., F.G.S.

3. " Further Notes on Rock-fragments from the South of Scotland imbedded in the Low-level Boulder-clay of Lancashire." By T. Mellard Reade, Esq., C.E., F.G.S.

In his paper on the Drift-beds of the North-west of England, Part II., Q. J. G. S. 1883, p. 119, the author noticed that the discovery of Criffel-granite erratics in the Lancashire drift first made by Mr. Mackintosh, had been confirmed by Mr. P. Dudgeon, from specimens forwarded by the author in 1882. In August of last year, he had an opportunity of travelling from Dumfries through Kirkcudbright to Wigtonshire, and of examining the rocks and the boulders derived from them. Two masses of granite have broken through Silurian strata in Kirkcudbright : the eastern of these granite masses forms the isolated mountain of Criffel, 1800 feet above the sea ; the western rises to 2331 feet, and is known as Cairnsmore of Fleet. The granite of the former is, as a rule, finer than that of the latter. Numerous boulders derived from both are found in the surrounding country.

The author pointed out in detail how different varieties of granite observed on Criffel and Cairnsmore of Fleet are clearly the rocks of which fragments are found in the drift of Lancashire ; and also showed that the Silurian " Greywackés " through which the granite of the mountains named has burst, are also represented by unmistakable specimens in the Lancashire Boulder-clay. The " Greywacké " varies in texture from a fine-grained sandstone to a coarse gritty sandstone, and in colour from dark blue and grey to deep purple-red. These beds, which belong to the Queensbury-grit gravels, are well seen in a line of cliffs called the Craigs of Garheugh, at the side of the road from Glenluce to Fort William. Specimens identical with these rocks have been found in the low-level Boulder-clay of various parts of Lancashire, as at Great Crosby, Innewick Fishery, and the Isle of Whithorn.

These identifications go far towards completing the identification of the rocks represented in the low-level Boulder-clay of Lancashire, and confirm the views already expressed by the author that

all stones in the Drift of north-western England are derived from the basins of the Irish Sea, and of rivers draining to it, except some stray fragments that may have come from the Highlands of Scotland.

4. "Ripple-marks in Drift." By T. Mellard Reade, Esq., C.E., F.G.S.

Amongst published notices of drift-deposits the author has never met with any description of ripple-marks, though, if the drift was formed under water, some should be found. In a spot to which his attention was called by Dr. Callaway, the Old Park Field sand-hole at Ketley, near Wellington, Salop, in a stratified drift-deposit, he had found early in 1883 three distinct beds of ripple-marked laminæ. One of the ripple-marks in the highest bed measured 9 inches from crest to crest and $1\frac{1}{4}$ inch in height, and had been produced by a wind from the N.W.

In July 1883 the author found ripple-marking in hard, fine loamy brown sand underlying a compact mass of Boulder-clay at Tranmere, Cheshire, in one of the approaches to the Mersey Tunnel. The marks were on a sloping bank, and the sand was faulted in places with a throw of from 2 to 4 inches. In the sand shell-fragments occurred, some of them being recognizable as those of *Turritella terebra*, *Cardium edule*, *Tellina balthica*, and a *Pholas*.

The position of this section in a hollow between higher ground was favourable to the preservation of ripple-markings. The beds undoubtedly are those named by the author the Low-Level Boulder-Clays and Sands.

March 5.—Prof. T. G. Bonney, D.Sc., F.R.S., President, in the Chair.

The following communications were read :—

1. "On the Structure and Formation of Coal." By E. Wethered, Esq., F.G.S., F.C.S.

The author, having referred to the work of previous investigators, pointed out that seams of coal do not always occur in one bed, but are divided by distinct partings, some of which, as in the case of the Durham main seam, contain *Stigmariæ*. It was important to notice this feature for several reasons, but especially as the beds of coal, defined by the partings, showed differences both in quality and structure. In the case of the shallow seam of Cannock Chase they had at the top a bed of coal 1 foot 10 inches thick, the brown layers of which were made up of macrospores and microspores. The bright layers were of similar construction, except that wood-tissue sometimes appeared; also a brown structureless material, which the author looked upon as bitumen. He, however, objected to that term, and thought that hydrocarbonaceous substance would be preferable. What this hydrocarbonaceous material originated from was a question for investigation. In the lower bed of the Welsh

"Four Feet" seam wood-tissue undoubtedly contributed to it; whether spores did was uncertain; it was true they could be detected in it. In the second bed of the shallow seam they had a very different coal from the upper one. It was made up almost as a whole of hydrocarbonaceous material. Very few spores could be detected. It was possible that the scarcity of these objects might be due to decomposition; but the author's investigations seemed to show that spores resisted decomposing influences more effectually than wood-tissue, which seemed to account for the fact that where they occur they stand out in bold relief against the other material composing the coal. Below the central bed of the shallow seam came the main division. In it the author detected a large accumulation of spores, but hydrocarbon formed a fair proportion of the mass. The author referred to other seams of coal from various parts of England, and pointed out the structure of each bed composing them. The conclusions on the evidence elicited from his investigations were (1) that some coals were practically made up of spores, others were not, these variations often occurring in the beds of the same seam; (2) that the so-called bituminous coals were largely made up of the substance which the author termed hydrocarbon, to which wood-tissue undoubtedly contributed.

An appendix to the paper, written by Prof. Harker, Professor of Botany and Geology at the Royal Agricultural College, Cirencester, dealt with the determination of the spores seen in Mr. Wethered's microscopic sections. Taking the macrospores, the resemblance to those of *Isoëtes* could not fail to strike the botanist. He had procured some herbarium specimens of *Isoëtes lacustris* in fruit, and compared the spores with those from the coal. When gently crushed, the identity of the appearance presented by these forms from the coal was very striking. The triradiate markings of the latter were almost exactly like the flattened three radiating lines which mark the upper hemisphere of the macrospores of *Isoëtes lacustris*. The writer therefore concluded that the forms in the coal were from a group of plants having affinities with the modern genus *Isoëtes*, and from this Isoëtoid character he suggested for them the generic title of *Isoëtoides*, pending further investigation.

2. "On Strain in connexion with Crystallization and the Development of Perlitic Structure." By Frank Rutley, Esq., F.G.S.

In a paper read before the Society and published in the 'Quarterly Journal' (vol. xxxvii. p. 391) some observations were made upon microscopic areas of depolarization in an obsidian tuff from Montana, U.S. The paper now read related to a further examination of similar phenomena in an obsidian from Java. The glass adjacent to the numerous crystals occurring in this rock exhibits depolarization, as in the case of the Montana tuff. In some instances a perlitic structure surrounds the crystals, and the depolarization then ends abruptly at the fissure. One instance is described in which such a fissure only partially encircles a crystal, and the depolarization is then seen to end abruptly at the fissure and also to

fade away gradually in those directions which are not thus limited. The conclusion was, that the depolarization is the result of strain, and that the perlitic fission is due to the same cause. It was also suggested that the development of the crystals may in some cases account for this strain, while in other instances similar evidence of strain is seen in perlitic areas where no crystal is visible. Other details concerning perlitic and spherulitic structure were also discussed.

3. " Sketches of South-African Geology. No. 1. A Sketch of the High-level Coal-field of South Africa." By W. H. Penning, Esq., F.G.S.

In this paper the author gave a sketch of the High-level Coal-field of the Transvaal and the neighbouring region. This coal-field was described as extending 400 miles from north to south, with an average breadth of 140 miles, so that its area is about 56,000 square miles. The tract consists of an elevated plateau forming the " High Veldts " of the Transvaal and the plains of the Orange Free State. It slopes away to the north-west, and is scarped to the south and east by the heights known as the Stormberg and Drakensberg mountains ; nearly all the principal rivers of South Africa take their rise in this tract of land. The coal-bearing beds forming the plateau rest unconformably in the north upon deposits probably of Upper Palæozoic age, described as the Megaliesberg beds. In the south-west the Lower Karoo beds underlie the coal-beds, also unconformably. The beds of the high grounds consist above of sandstones, called the " High Veldt beds " by the author, and below of shales, for which the name of " Kimberley beds " is proposed, after the chief town of Griqualand West, in which district they form nearly the whole surface. These two series are conformable, and generally lie horizontally. In the shales coal occurs only in minute patches ; the seams of coal are interstratified with the sandstones, into which the shales pass up gradually, and which sometimes include thick-bedded grits and conglomerates. Both shales and sandstones contain interstratifications and numerous dykes of trap, which have rarely produced much alteration in the sedimentary beds, from which the author concludes that the eruptions were subaqueous and contemporaneous or nearly so. Owing to the persistent horizontality of the rocks, the mountains and valleys are merely carved out of the plateau, so that the thickness of the deposits is easily measured. The author gave 2300 feet as the minimum thickness of each series. By a comparative section it was shown that the coal-bearing sandstones (" High Veldt beds ") are the " Upper Karoo " of Stow, and the " Stormberg beds " of Dunn. The " Kimberley beds " are the Upper Karoo beds of Dunn.

In the latter part of his paper the author noticed briefly the different localities where coal has been found, namely, Newcastle, Lange's Nek, the Lebelelasberg mountains, near New Scotland, several places on the High Veldt, Wemburg, Brandfoote, Cornet Spruit, Burgersdorf, and Indwe, twenty miles east of Dordrecht. The most northerly point of the Transvaal where coal has been found

is on the Letsebo river. West of the Drakensberg coal occurs at a lower level.

<div align="center">March 22.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.</div>

The following communications were read :—

1. " On *Rhytidosteus capensis*, Owen, a Labyrinthodont Amphibian from the Trias of the Cape of Good Hope." By Sir Richard Owen, K.C.B., F.R.S., F.G.S.

2. " On the Occurrence of Antelope-remains in Newer Pliocene Beds in Britain, with the Description of a new Species, *Gazella anglica*." By E. Tulley Newton, Esq., F.G.S.

3. " A Comparative and Critical Revision of the Madreporaria of the White Lias of the Middle and Western Counties of England, and of those of the Conglomerate of the Base of the South-Wales Lias." By Robert F. Tomes, Esq., F.G.S.

<div align="center">XXI. *Intelligence and Miscellaneous Articles.*</div>

ON THE ELECTROLYSIS OF SOLID GLASS. BY E. WARBURG.

THE facts described in this paper may be summarized in the following manner :—

In the electrolysis of lime-soda glass heated to about 300° between mercury electrodes, a badly conducting layer of silicic acid is formed on the anode side of the glass, which soon reduces the strength of the current to a fraction of its original value. This layer has a greater or less thickness, according as a greater or lesser electromotive force has acted in the circuit in a definite time. It is visible, showing the colours of thin plates, diminishes the surface-conductivity of the glass in the cold to a fraction of its original amount, and at a high temperature, when the mass of the glass has become a conductor, it acts like the dielectric of a condenser whose coatings are the conducting mass of the glass, and the mercury of the anode. The capacity of this condenser was found to be independent of the difference of potentials of the coatings, between 1 and 20 Bunsen's elements ; and for a square centimetre of the glass used it varied from 0·021 to 0·041 microfarad, according as the layer was formed by 30 or 15 Bunsen's elements acting for several hours at 300°.

The formation of this layer may be avoided by using sodium amalgam as anode ; the result of the electrolysis may then be quantitatively determined. In this a quantity of sodium is given off at the kathode and absorbed at the anode, so that the weight of the glass does not vary ; the weight of the sodium is chemically equivalent to the weight of the silver which is deposited at the same time in the silver voltameter. During electrolysis the glass remains perfectly clear ; and it was found that all the properties of the

glass were not appreciably altered by electrolysis.—Wiedemann's *Annalen,* No. 4, 1884.

ON PHENOMENA OF DIFFRACTION IN MOIST AIR.
BY M. KISSLING.

In a thorough experimental investigation into the influence which foreign admixtures exert on the formation of fog in moist air—an influence first established by Coulier and Mascart, and then by Aitkin—the author has observed a series of phenomena of diffraction, the development of which, and the law of whose formation, can only with difficulty be made to agree with Fraunhofer's law of the phenomena of diffraction; they are, on the other hand, in obvious connexion with the phenomena of twilight, which have recently excited such universal interest. The author only gives briefly the most important results of his experimental investigation.

The phenomena are produced in a tube closed by two parallel glass plates, through which the diaphragm of an Argand burner placed at a suitable distance was observed.

The author found that Aitkin's law was in general confirmed, namely, that when aqueous vapour is condensed in the air, this always takes place on some solid nucleus. Thus, in the ordinary unfiltered air of a dwelling-room, where the space in which diffraction occurs is but slightly cooled, the fog is so strong that it greatly enfeebles even a powerful source of light. If the unfiltered air be gradually admixed with filtered air, the formation of fog gradually diminishes, while at the same time phenomena of diffraction set in, the intensity of whose colour increases until the quantity of vapour has sunk to a certain, extremely small amount. As the filtration is continued, the coloured phenomena become rapidly less intense, and a formation of fog can no longer be perceived. It must be observed that by "vapour" the author understands the totality of all foreign constituents in atmospheric air with the exception of water. If the degree of moisture in the diffraction-space is diminished, so that it is only slightly removed from its point of saturation, an exceedingly rapid decrease of the production of colour sets in. It is found in general that the absolute maximum of the phenomena of diffraction is conditioned by the coincidence of that amount of vapour which is most favourable to light, with the maximum moisture in the layer in question.

Small admixtures of SO_2 and NH_3 with the unfiltered air of a room produce so strong a fog, that any action of diffraction ceases.

Finely divided dust of pumice from Krakatoa exerted a perceptible, though small, influence on the formation of fog.— *Beiblätter der Physik,* vol. viii. p. 514.

XXII. *On the Spectral Lines of the Metals developed by Exploding Gases.* By G. D. Liveing, *M.A., F.R.S., Professor of Chemistry,* and James Dewar, *M.A., F.R.S., Jacksonian Professor, in the University of Cambridge*[*].

NOT long since Berthelot published the results of some investigations, by means of a chronograph, of the rate of propagation of the explosion of mixtures of oxygen with hydrogen and other gases. He found that in a mixture of oxygen and hydrogen in the proportions in which they occur in water, the explosion progressed along a tube at the rate of 2841 metres per second; not far from the velocity of mean square for hydrogen particles, on the dynamic theory of gases, at a temperature of 2000°.

This is a velocity which, though very far short of the velocity of light, bears a ratio to it which cannot be called insensible. It is in fact about $\frac{1}{105000}$ part of it. Hence if the explosion were advancing towards the eye, the waves of light would proceed from a series of particles lit up in succession at this rate. This would be equivalent to a shortening of the wave-length of the light by about $\frac{1}{105000}$ part; and in the case of the yellow sodium lines would produce a shift of the lines towards the more refrangible side of the spectrum by a distance of about $\frac{1}{107}$ of the space between the two lines. It would require an instrument of very high dispersive power and

sharply defined lines to make such a displacement appreciable. With lines of longer wave length than the yellow sodium lines, the displacement would be proportionately greater. Further, if a receding explosion could be observed simultaneously with an advancing explosion, the relative shift of the line would be doubled, one image of the line observed being thrown as much towards the less-refrangible side of its proper position as the other was thrown towards the more-refrangible side. The two images of the red line of lithium would in this way be separated by a distance of about $\frac{1}{8}$ of a unit of Ångström's scale; a quantity quite appreciable, though much less than the distance between the components of b_3, and about equal to the distance of the components of the less refrangible of the pair of lines E. We thought therefore that we might test theory by experiment.

A preliminary question had, however, to be answered. What lines could be seen in the flash of the exploding gases? We were pretty certain that the hydrogen lines could not be seen, but that probably we might get sufficient dust of sodium compounds floating in the gas to make the sodium lines visible. A preliminary observation was made on the flash of mixed hydrogen and oxygen in a Cavendish's eudiometer, which showed not only the yellow sodium lines, but the orange and green bands of lime and the indigo line of calcium all very brightly, as well as other lines not identified. The flash is very instantaneous, but nevertheless produces a strong impression on the eye ; and by admitting the light of a flame into the spectroscope at the same time as that of the flash, the identity of the lines was established. That sodium should make itself seen was not surprising, but that the spectrum of lime should also be so bright had not been anticipated. At first we thought that some spray of the water over which the gases were confined must have found its way into the eudiometer ; but subsequent observations led us rather to suppose that the lime was derived from the glass of the eudiometer. The lime-spectrum made its appearance when the eudiometer was quite clean and dry, and when the gases had been standing over water for a long time.

To obtain the high dispersion requisite, as already explained, we made use of one of Rowland's magnificent gratings, with a ruled surface of $3\frac{1}{8}$ by $2\frac{1}{8}$ inches, and the lines 14,438 to the inch. One telescope fitted with a collimating eyepiece served both as collimator and observing-telescope; and by this means we were able to use the spectra of the third and fourth orders with good effect.

Observations were made with this instrument on explosions

in an iron tube shown in section in fig. 1, half an inch in
diameter, fitted at the end with a thick glass plate (*a*), held on
by a screw-cap (*c*) and made tight with leaden washers.
Small lateral tubes (*d d*), at right angles to the main tube, were
brazed into it near the two ends, for the purpose of connect-
ing it with the air-pump, admitting the gases, and firing
them. For this last purpose a platinum wire (*b*) fused into
glass was cemented into the small tube, so that an electric
spark could be passed from the wire to the side of the small
tube when the gases were to be exploded.

fig.1.

fig.2.
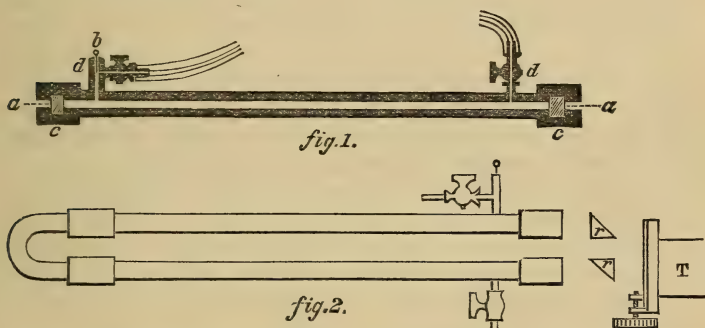
To bring out the lithium lines, a small quantity of lithium
carbonate in fine powder was blown into the tube before the
cap with glass plate was screwed on. Powder was used
because we supposed that it must be loose dust which would
be lighted up by the explosion. The lithium lines came
out bright enough, and it was unnecessary to put in any more
lithium for any number of explosions. The tube was of
course quite wet after the first explosion from the water
formed, but the lithium lines were none the less strong.
Indeed, after the tube had been very thoroughly washed out, the
lithium lines continued to be visible at each explosion, though
less brightly than at first. A good deal of continuous spec-
trum accompanies the flash which, from the overlapping of
spectra of different orders, makes observations difficult, so a
screen of red glass was used to cut this off when the lithium
red line was under observation. In any case, however, close
observation of the flashes is very trying, from the suddenness
with which the illumination appears and the briefness of its
duration. At first we compared the lithium line given by the
flash of the exploding gases with that produced by the flame
of a small Bunsen burner in which a bead of fused lithium
carbonate was held, both being in the field at once. While
the flame-line was sharply defined, the flash-line had a different

M 2

character and was always diffuse at the edges; so that it was not possible in this way to substantiate the minute difference of wave-length indicated by theory, though the flash-line certainly seemed a little the more refrangible of the two.

We then tried taking the explosion in a tube bent round so as to be returned upon itself, the two parts of the tube being parallel to each other, and the glass ends side by side (fig. 2). The axis of the collimator (T) was made to coincide with that of one limb of the tube, so that the flash in that limb was seen directly; and by means of two reflecting prisms (*r, r*) the light from the other limb was thrown into the slit, and the two images were seen simultaneously one above the other. As the gas was ignited from one end of the tube, the flash was seen receding in one limb, approaching in the other, so that the displacement of the two lines would be doubled. Still we were unable to substantiate any relative displacement of the lines on account of their breadth and diffuse character. By washing out the tube the breadth of the lines was considerably reduced, but they remained diffuse at the edges, and baffled any observation sufficiently accurate to establish a displacement. Certainly there appeared to be a very slight displacement, but it was not so definite that one could be sure of it.

These observations, however, led us to some other interesting results. In the first place, one of the two images of the lithium line almost always was reversed—that is, showed a dark line down the middle. This was the line given by the flash approaching the slit. The receding flash in the other limb of the tube gave as broad a bright line, but it had no dark line in its middle. This observation was made a great many times; and the fact of the reversal established independently in the case of some other metallic lines by means of photographs. These reversals show that in the wave of explosion the temperature of the gases does not reach its maximum all at once; but the front of the wave is cooler than the part which follows and absorbs some of its radiation, while the rear of the wave does not produce the same effect. One would suppose that there must be cooler lithium-vapour in the rear of the wave as well as in its front; but it is possible that the absorption produced by it extends over the whole width of the line, and not only over a narrow strip in the middle. For we observed that when a little lithium carbonate was freshly put into the tube, the red line was so much expanded as to fill the whole field of view—that is to say, it was some ten or twelve times as wide as the distance between the two yellow lines of sodium; but by washing out the tube with water

(that is, by reducing the quantity of lithium present in the tube), the line could be reduced in width until it was no wider than one tenth of the distance between the two sodium lines. This seems to prove that the breadth of the line is directly dependent on the amount of lithium present.

M. Fievez has, in a recent publication (*Bulletins de l'Académie royale de Belgique*), concluded, from observations on sodium, that the widening of the lines is solely due to elevation of temperature. The flash of the exploding gases cannot be raised in temperature by the presence of a minute quantity more of a lithium compound; so that in our case the widening cannot be ascribed to any thing but the increase in the quantity of lithium present, or to some consequence of that increase. It is not improbable that the amount of lithium vaporized in the front of the wave of explosion is less than in the following part, and hence the absorption-line is not so wide as the bright line behind it, while in the rear of the wave the absorption extends over the whole width of the bright band, and so is not so easily noticed. Only twice amongst many observations was any reversal of the lithium line seen in the receding wave of explosion.

On observing the flash with a spectroscope of small dispersion instead of that with the grating, the continuous spectrum was very bright, but the metallic lines stood out still brighter; not only the red line of lithium, but the orange, the green, and the blue lines were very bright, and continued so when the pressure of the gases before explosion was reduced from one atmosphere to one third of an atmosphere. The violet line was not seen, but it may have been so much expanded as to be lost in the continuous spectrum; for it showed in a photograph afterwards taken. Other lines were, however, seen—the sodium yellow lines, the calcium indigo line, a group of other blue lines, and a group of green lines, amongst which one line was conspicuous, and this line, by comparison with the solar spectrum, was identified with E. We had not expected to see any lines of iron, as iron and its compounds give no lines in the flame of a Bunsen burner, and we supposed that it would only be volatilized at a much higher temperature. But the appearance of E suggested that other of the green and blue lines might be due to iron; so we proceeded to compare the positions of these lines with those of the electric spark between iron electrodes. For this purpose one of the spark-lines was first brought carefully on to the pointer, or cross wires, in the eye-piece of the observing telescope, and then, the passage of the spark being stopped, the flash of the exploding gases was observed. It was not diffi-

cult to see whether any line was on the pointer; and the observation could be repeated as many times as was desired without any shift of the apparatus. Nine of the most conspicuous green and yellowish-green lines in the flash were thus identified with lines of iron. For the blue and violet we adopted the photographic method as much less trying to the eyesight. Eight to twelve flashes were taken in succession without any shift of the apparatus, so as to accumulate their effects on the photographic plate. Eight flashes were found enough in general to produce a good impression, and more than twelve could not well be taken without turning out the water which accumulated in the tube, and cleaning the glass which closed its end. After the flashes had been taken, but without shifting the photographic plate, the slit of the spectroscope was partly covered, and the electric spark between iron points passed in front of the slit. We had thus on the plate the photograph of the flash as well as of the spark. Fourteen more lines in the indigo and violet were thus identified with iron lines; and on extending the photographs into the ultra-violet, and substituting quartz lenses and prisms for the glass ones hitherto used, a much larger number of lines were identified. There could be no doubt, then, that we had iron vapour in the flash. We supposed that it must be derived from dust of oxide shaken by the explosion off the sides of the tube, and we had the tube bored out clean and bright like a gun-barrel. This made no diminution in the brightness or number of the lines; and we came to the conclusion that the explosion detached particles of iron from the tube, and converted them into vapour. This was confirmed by finding that, however carefully the tube had been cleaned, the glass ends always became clouded with a rusty deposit after ten or twelve flashes. Altogether 68 lines of iron have been identified in the flash, of which about 40 lie in the ultra-violet between H and O. Only one iron line above O has been definitely identified, and that in only a few photographs. It is T.

As iron gave so many lines in the flash it was reasonable to suppose that more volatile metals would give their lines too. Linings of thin sheet copper, lead, cadmium, zinc, aluminium, and tin were successively put into the tube, and their effects on the flash observed. Copper gave one strong line in the green (wave-length 5104·9), but no other line in the visible part of the spectrum. In the ultra-violet two strong lines between Q and R came out in the photographs, frequently as reversed lines. Some of the photographs showed also something of the shaded bands in the blue which are

ascribed to the oxide of copper. The green line of copper had been observed in the flash before the copper lining was put into the tube; and we concluded that the copper was derived from the brass with which the small lateral tubes were fastened into the large tube, or that the iron of the tube contained a little copper. When the leaden lining was used, only one visible line of lead was developed, and that was the strong violet line, but two ultra-violet lines between M and N were strongly depicted on the photographic plates. The violet line of lead had also been observed in many of the photographs taken before the leaden lining was introduced. This we ascribed to the leaden washers used to make the glass or quartz plates air-tight. The line was greatly increased in strength by the leaden lining. The zinc lining gave no visible line at all, notwithstanding the easy volatility of the metal; and in the ultra-violet it gave only a very doubtful impression of one of the lines near P. The cadmium, aluminium, and tin linings gave no lines at all. Zinc dust put into the tube gave no zinc lines, merely increased the continuous spectrum, and speedily rendered the quartz end opaque.

A clean wire of magnesium put into the tube gave the *b* group of lines, but no other line. No trace of the blue line, so conspicuous in the flame of burning magnesium, nor of the triplets near L and S, nor of the very strong line, the strongest of all in the arc, at wave-length 2852. b_1 and b_2 were well seen; but as b_4 is an iron line, as well as a magnesium line, and the iron line was visible in the flash before the magnesium wire was introduced, we cannot be sure whether the magnesium line, as well as the iron line, was present in the flash. Magnesia did not develop any line at all; merely augmented the continuous spectrum.

Compounds of sodium, such as the carbonate and chloride, introduced in powder gave the ultra-violet line between P and Q strongly, frequently reversed; but no other line except of course D. Potassium compounds developed, often reversed, the pair of violet lines, and also the ultra-violet pair near O, but no others.

A strip of silver developed two ultra-violet lines, one on either side of P; but we could not detect in the flash the well-known green lines of that metal. When powder of silver oxalate was introduced, the yellowish-green line (w.l. 5464) was seen at the first explosion but not afterwards. As silver oxalate is itself an explosive compound, decomposing with an evolution of heat, it is reasonable to ascribe the appearance of this line at the first explosion to the extra temperature so engendered.

Strips of copper, electro-plated with nickel, brought out almost all the strong nickel lines in the ultra-violet between K and Q; 25 were photographed. When nickel oxalate was put in so as to give a powder of metallic nickel after the first explosion, the same lines were developed, and three additional lines in the ultra-violet. Only one line was seen in the visible part of the spectrum, and that was the yellowish-green line (w.l. 5476).

Copper wires electro-plated with cobalt gave in the flash 22 lines in the violet and ultra-violet, between G and P; no lines beyond those limits. Cobalt oxalate gave no more.

No other metal gave anything like so many lines as iron, nickel, and cobalt; and it is remarkable that almost all the lines of these metals developed in the flash lie in the same region between G and P.

We expected that manganese would have given several lines in the flash; but it was not so. Neither metallic manganese, nor any of several compounds which we tried, gave us any lines of that metal except the violet triplet, and this was generally given by the iron tube alone, and was merely stronger for the manganese put in. The green channellings characteristic of manganese, and ascribed to the oxide, were, however, well seen when metallic manganese was used.

Chromium, introduced as bichromate of ammonia, which of course became chromium oxide at the first flash, gave three triplets in the green, the indigo, and the ultra-violet near N respectively, but no other lines.

Bismuth, antimony, and arsenic gave no lines, nor did mercury spread over a sheet of copper lining the tube. Several metals were tried as amalgams spread over such a piece of copper, but with no fresh results, except in the case of thallium, which gave the green line strongly, the strong line between L and M, and two lines between N and O.

On the whole it does not appear that the form in which the metal is introduced into the tube makes much difference. The merest traces of those which gave lines were sufficient. Generally when a metal had been put into the tube, its lines continued to show after the strip or lining had been removed. Thus, after the nickel strips had been taken out, and the tube cleaned out as completely as it could be mechanically, the nickel lines still came out in the flash, and the same was the case with other metals.

The strongest part of the water-spectrum, from *s* to near R, generally impressed itself more or less on the photographic plate; but, with the exception of T, which was only developed once or twice, no lines made their appearance in the region more refrangible than *s.*

Thus far the experiments had been made with the gases at the atmospheric pressure, or nearly so, before ignition. The proportions of hydrogen and oxygen were nearly two to one; but an excess of either gas to the extent of one fifth did not sensibly affect the results.

Other explosive mixtures were tried. Carbonic oxide with oxygen, and marsh-gas with oxygen, developed in general the same lines as the hydrogen mixture, but gave a much brighter continuous spectrum. Sulphuretted hydrogen, arseniuretted hydrogen, and antimoniuretted hydrogen, exploded with oxygen, also gave very bright continuous spectra, but no lines attributable to sulphur, arsenic, or antimony.

We have also tried explosions at higher pressures ; mixtures of hydrogen, carbonic oxide, and marsh-gas respectively, with oxygen, were compressed into the tube by a condensing syringe until the pressure reached two and a half atmospheres, and in some cases three and a half atmospheres. The general effect of increasing the pressure was to strengthen very much the continuous spectrum, and also to intensify the bright lines, so that photographs could be taken with a smaller number of explosions. The lines previously observed to be reversed were more strongly reversed, but no new lines which we can attribute to the metals employed were noticed. No iron line more refrangible than T showed itself in the photographs. But a banded spectrum, of which traces had been noticed in the flash of the gases at lower pressure, came out decidedly. This spectrum occupies the region between P and R ; it is not a regularly channelled spectrum, though probably under higher dispersion it would resolve itself into groups of lines like the water-spectrum. In fact it seems to us most probable that it is a development of the water-spectrum, dependent on the pressure.

It seems very remarkable that metals so little volatile as iron, nickel, and cobalt should develop so many lines [*] in the flash, while more volatile metals show few or no lines. We do not know that any lines attributed to the metals, as distinct from their compounds, which have been observed in the gas-flame cannot be seen also in the flash of the exploding gases, unless they be the blue lines of zinc which Lecoq de Boisbaudran has seen faintly in the gas-flame when zinc chloride was introduced. These are, however, so faint in the flame, that they might easily escape notice in the much stronger continuous spectrum of the flash. But iron, nickel, and cobalt show no lines of those metals in a gas-flame. Mitscherlich (*Ann. d. Phys. u. Chem.* Bd. 121, St. 3), by

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[*] For detailed list of these lines see Proc. Roy. Soc. vol. xxxvi. pp. 473-5.

mixing vapour of ferric chloride with the hydrogen burnt in an oxyhydrogen-jet, obtained a number of the lines of iron. These form three groups—one below D, one near E, and one near G. The last two groups have a general correspondence with the lines developed in the explosions in the visible part of the spectrum; but exact identification is not possible with his figure. Of other metals he seems also to have found the same lines in the oxyhydrogen-jet which we have seen in the explosions, but with additional lines in several cases. Thus he found three zinc and as many cadmium lines, two of mercury, four of copper, and so on.

Gouy (*C. R.* 1877, p. 232) has observed in the inner green cone of a modified Bunsen burner fed with gas mixed with spray of iron-salts, four green lines of iron which we did not find in the flash. He saw two of the blue lines, but not the other lines which we have noticed. In like manner with cobalt, he observed two feeble blue rays which we did not see in the explosions; also one zinc, one cadmium, and one silver line which we did not see; and he did not notice the green copper line which we always have seen in the explosions. In other cases he has noticed the same lines that we have noticed.

Comparing the spectrum of the explosions with that of iron wire burnt in a jet of coal-gas fed with oxygen, they may be called identical. We find in them generally the same lines and the same relative strengths of the lines. For instance, in the explosion-spectrum the strength of the groups of lines on either side of M and the line at wave-length 3859·2 is decidedly greater as compared with the other lines than it is in the arc-spectrum of iron. It is the same in that of iron burnt as above mentioned. T, however, comes out more strongly in the last-mentioned spectrum than in the explosions.

German-silver wire burnt in the coal-gas and oxygen jet gave the same nickel and copper lines as were developed in the explosions. Silver wire gave in the same jet the two silver lines near P, but no channelled spectrum. Spray of cobalt chloride gave also the same lines as in the explosions, with a few additional; while spray of manganese chloride gave the strong manganese triplet at wave-length about 2800, more refrangible than anything observed in the explosions, besides the usual violet triplet.

On the whole the spectra produced by the jet of coal-gas and oxygen are very similar to those of the explosions as far as the metallic lines go; they exhibit a few more lines, or it may be these are more easily observed.

Of the green and blue lines of iron seen by us in explosions nine are registered by Watts as occurring in the flame of a Bessemer converter ; or at least the lines he gives are so near that we cannot doubt their identity.

When we come to make a comparison with the spectrum of the spark-discharge from a solution of ferric chloride, the differences become more marked. Not only are there many more lines in the spark-spectrum, but the relative intensities of those lines which are common to both spark and explosion are very different, and two of the iron lines seen in the explosions appear to be absent from the spark. The differences between the spectrum of the spark taken from a liquid electrode and that given by solid electrodes has usually been attributed to the lower temperature of the former ; but the absence from the former spectrum of the line at wave-length 4132, and the feebleness of the line at wave-length 4143, both strong lines in the arc and in the explosions, as well as in the spark between solid electrodes, seem to indicate that the differences of spark-spectra are not simply due to differences of temperature. In fact we know so little about the mechanism, so to speak, of the changes of electric energy into heat, and of heat into radiation, that there is no good reason for assuming that the energy which takes the form of radiation in the electric discharge through a gas must first take the form of the motion of translation of the particles on which temperature depends. The gas may, for a short time, be intensely luminous at a very low temperature ; and if the impulses which give rise to the vibratory movements of the particles be of different characters, the characters of the vibrations also may differ within certain limits.

Leaving, however, the realms of speculation, we may mention that we have before observed the spectrum of iron at a temperature intermediate between that of the oxyhydrogen-jet and that of the electric arc.

Some time since (Proc. R. S. xxxiv. p. 119, and Proc. Camb. Phil. Soc. iv. p. 256) we described the spectrum proceeding from the interior of a carbon tube strongly heated by the electric arc playing on the outside. This spectrum approaches more nearly to that of the arc inasmuch as it shows all, or almost all, the iron lines given by the arc between F and O, and the aluminium pair between H and K ; but it resembles the explosion-spectrum in the relative strength of some of the iron lines, and in the absence of almost all iron lines between O and T. The iron lines seen reversed against the hot walls of the carbon-tube correspond with the strongest of the explosion-lines ; the strong lines near M and a little below L in

the explosions being those most strongly reversed in the photographs of the carbon-tube. The greater completeness and extent of the iron spectrum, as well as the presence of the aluminium lines, which are entirely wanting in the explosion-spectrum, indicate that the temperature of the tube was higher than that of the explosion. That iron, nickel, and cobalt are volatile in some degree at the temperature of the explosion appears to be proved, and makes the appearance of iron lines at the very apices of solar prominences, as observed by Young, less astounding than it seemed to be at first sight. The ascending current of gas making the prominence may very well carry iron vapour with it; or we may not unreasonably suppose that there is meteoric dust containing iron everywhere in the outer atmosphere of the sun, which becomes volatilized, and emits the radiation observed, when it is heated up by the hot current of the prominence. What the temperature of such a current may be we cannot well gauge, but it is high enough to give the hydrogen-spectrum, of which no trace has been observed in the flash of the explosions or in the oxyhydrogen-jet. The temperature of the explosions we know with tolerable accuracy, at least when the gases are at atmospheric pressure to begin with. Bunsen (Phil. Mag. 1867, p. 494) found the pressure of the explosion was for hydrogen and oxygen 9·6 atmospheres, and for carbonic oxide and oxygen 10·3 atmospheres, and he calculated the corresponding temperatures to be 2844° and 3033°. Recently published observations by Berthelot and Vieille (*Comptes Rendus*, 1884, p. 548) put the pressure of explosion of oxygen and hydrogen at 9·8 atmospheres and of carbonic oxide and oxygen at 10·1, and the corresponding temperatures 3240° and 3334°. The pressures determined by the two observers agree closely, and the calculated temperatures are not very discordant. On the whole, we cannot be wrong in assuming the temperature of the exploding gases to be about 3000°; and we see that at this degree such metals as iron, nickel, and cobalt are vaporous and emit many characteristic rays, and that by far the greatest part of these rays lie between narrow limits of refrangibility G and P. Even for other metals there is a predominance of rays in the same part of the spectrum. The lines of lead, potassium, and manganese, three out of four lines of thallium, and two thirds of those of chromium, observed in the explosions, fall within the same region. It must not be inferred that these facts indicate the limit of the rate of oscillation which can be set up in consequence of an elevation of temperature to 3000°, because we know that the spectrum of the

lime-light extends much further. But it might be possible to establish a sort of spectroscopic scale of temperatures if the lines which are successively developed as the temperature rises were carefully noted. Thus the appearance of the iron line T seems to synchronize with temperature of about 3000°. The lithium blue line is invisible in the flame of an ordinary Bunsen burner, but is just visible at the temperature of the inner green cone formed by reducing the proportion of gas to air in such a burner, while in the exploding gas the green line too is seen. It seems to need a temperature above 3000° to get the aluminium lines at H. Probably no line is ever abruptly brought out at a particular temperature—it will always be gradually developed as the temperature rises; yet the development may be rapid enough to give an indication which may be useful in default of means of more exact measurement. In former papers treating of spectroscopic problems (Proc. Roy. Soc. vol. xxxiv. p. 130, and xxix. p. 489) we have more than once adverted to the necessity of the study of the spectra both of flames and of the electric discharge under modified conditions of pressure. The projected experiments on the arc in lime-crucibles have not yet been carried out; but the present is a first instalment of a study of flame-spectra under such conditions.

XXIII. *On Normal Elements for Electrometric Measurements.* *By* H. W. Beetz[*].

IN order to measure a difference of potential in absolute units a normal element is required, having a perfectly definite electromotive force, which can either be put together once for all, or can always be set up in exactly the same way and without too much trouble. According to Kittler's experiments[†], a Daniell element, having a porous cell, does not at all fulfil these conditions, since its electromotive force is subject to continuous change. On the other hand, an element composed of chemically pure zinc and pure copper, in dilute sulphuric acid and copper-sulphate solution of definite strength, the solutions being placed in connexion by means of a siphon-tube terminating in small openings and filled with the same sulphuric acid, has always the same electromotive force, and since it can easily be put together, forms

a convenient standard cell. Using concentrated copper-sulphate solution and dilute sulphuric acid of specific gravity 1·075, Kittler found the electromotive force of such an element to be 1·195 volt, which decreased to 1·059 volt when the dilute sulphuric acid was replaced by concentrated zinc-sulphate solution.

Of the Daniell elements hitherto employed for measurement of difference of potential, that of Raoult[*] best fulfils the conditions here laid down; that of Lodge[†], employing dilute zinc-sulphate solution, less satisfactorily; whilst combinations containing porous cells, such as that proposed by Buff[‡], are still less suited to serve as normal elements.

But none of these are able to maintain a constant electromotive force, as is now desirable for electrometric measurements, since in all gradual diffusion of the liquids takes place. I myself[§] have formerly made use of similarly arranged normal elements, for measurements made according to the compensation-method; but they do not answer for electrometric measurements, and I have therefore been obliged continually to renew the element. For the length of time during which unbroken observation with the electrometer is usual, we may rely upon the constancy of the element.

The frequent putting together and taking apart of an element is a labour always willingly avoided. Hence the permanently-connected zinc and mercury element of Latimer Clark[||] was gladly welcomed. Its electromotive force (1·457 volt) was found nearly constant in different preparations of the element according to the method described. But it has two undesirable properties: the one is the great variation of electromotive force with change of temperature, which, however, is easily allowed for in calculation, but which does not exist[¶] in the case of the Daniell elements; the other is the great decrease which the electromotive force suffers if the circuit is closed even for a very short time. This may easily occur. An unintentional contact in some of the auxiliary apparatus employed in the measurements, for example in the key which I have described[**], is sufficient to render the element useless for one or several days. I obtained a diminution of electromotive force, amounting to 2 per cent., in a Latimer-Clark

 * *Ann. de Chim. et de Phys.* [4] ii. p. 345 (1864).
 † Phil. Mag. [5] v. p. 1 (1878).
 ‡ Lieb. *Ann.* lxxxv. p. 4 (1853).
 § Wied. *Ann.* iv. p. 5 (1878).
 || Proc. Roy. Soc. xx. p. 444 (1878); *Beibl.* ii. p. 565 (1878).
 ¶ Kittler, *loc. cit.* p. 371.
 ** Wied. *Ann.* x. p. 371 (1880).

element in which the circuit had been closed for only half a minute. A Daniell element would have shown scarcely any change under similar conditions.

But this defect of the Latimer-Clark element may be almost entirely remedied by giving to the cell so great a resistance that only an insignificant current can be generated.

A U-tube of 1 centim. diameter and legs 75 centim. long was filled with the paste of mercury-sulphate and zinc-sulphate solution, prepared according to the instructions, but heated so much that after cooling it became hard. The paste was boiled in the tube by means of a water air-pump. The zinc pole was introduced into the upper end of the tube and the mercury pole into the lower, and the openings were closed with paraffin. The element is very convenient for use on the laboratory-table, since the two poles may pass through holes bored in the table, the whole body of the tube being protected underneath the table. The internal resistance of the element was 15,700 ohms*. Its electromotive force was somewhat smaller than given by Latimer Clark. If, in fact, the electromotive force of a normal Daniell cell (with dilute sulphuric acid) be taken as 1·195 volt, then that of my mercury element was 1·442 volt (instead of 1·457 volt). When the element was short-circuited, its electromotive force was as follows:—

After 5 minutes	.	.	.	1·440 volt.
,, 1 hour	.	.	.	.	1·439	,,
,, 4 hours	.	.	.	.	1·439	,,
,, 6 ,,	.	.	.	.	1·437	,,
,, 12 ,,	.	.	.	.	1·434	,,
,, 48 ,,	.	.	.	.	1·408	,,

We see therefore that the element resists the influence of polarization for a long time. Polarization could indeed only be very slight, since the current which passed through the element has only the intensity of 0·000091 ampere. The electromotive force only diminished 2 per cent. after use for 48 hours, a decrease which is very small indeed compared with the falling off in the usual form of the Latimer-Clark element. It is easy to avoid short-circuiting the element for such a length of time; but if the element has once become enfeebled, it recovers itself only slowly. Thus, after 24 hours I found its strength to be 1·430 volt.

The idea of replacing the fluid of an element by a solid body may be carried out also with a Daniell element. Fine alabaster plaster-of-Paris was mixed with concentrated copper-

* The resistances were measured by my first assistant, Dr. Pfeiffer, by the use of alternate currents.

sulphate solution to about the consistency employed in making plaster casts, and some more with concentrated zinc-sulphate solution. A U-shaped glass tube, of 4 millim. diameter and with legs 22 centim. long, was partly filled with the one paste, and after it had set was filled up with the other, so that the two were in close contact. A copper wire was introduced into the copper paste before it had set, and a zinc wire into the zinc paste. The upper part of each leg was cleared from plaster and filled up with paraffin.

Several dry Daniell elements thus prepared were compared with an element put together with concentrated solutions of copper sulphate and zinc sulphate, and tested in respect of the effect of change of temperature and of short-circuiting. Taking the electromotive force of the liquid element as equal to unity, the three dry elements I., II., and III. gave, when measured on different days:—

I.	II.	III.
0·996	0·993	1·000
0·998	0·996	0·996
1·000	0·999	0·993
...	0·998	0·998
Mean . . 0·998	0·996	0·997

The temperature varied in all these observations by a few degrees only; the small apparent variations in the electromotive force of the dry elements are partly at least accounted for by small changes in the electromotive force of the fluid element, which was put together fresh each time. On the whole, however, the dry element is a little weaker than the fluid element; it contains no amalgamated zinc, because such amalgamated wires are very brittle.

A second series of experiments was concerned with the influence of temperature. The elements II. and III., sometimes at the temperature of the air, sometimes in baths of different temperatures, were compared with the fluid element, which had always a temperature of nearly 20 °C. On account of the small conducting-power of the dry elements for heat, they remained always three quarters of an hour in the bath before the measurements were made. If the electromotive force of the fluid element is again taken as unity, that of the dry element was as follows:—

	II.			III.
At 0°	0·996		At 1°	1·007
„ 20	0·993		„ 21	1·000
„ 39	0·983		„ 32	0·995
			„ 55	0·981

The decrease in electromotive force of each of the two elements for low temperatures between 0° and 20° amounted to only 0·015 per cent. for an increase in temperature of 1°. But the temperature-coefficient increases with increase of temperature. With element II. it amounted to 0·053 between 20° and 30°; with element III. to 0·045 between 21° and 32°, and between 32° and 55° even to 0·061. For Latimer-Clark's element, Helmholtz and von Kittler* agree in finding it to be 0·08. Within the narrow limits within which electrometric measurements are commonly made, the influence of temperature upon the electromotive force of the dry Daniell element may be altogether neglected.

The effect of short-circuiting is seen from the following experiments made with elements I., II., III.

The element was short-circuited for a certain length of time, then contact was broken, and the difference of potential measured. We do not thus obtain actually the lowest value which the difference of potential may attain, since this increases even during the few seconds which the measurement requires; but we do obtain the value with which we are actually concerned in our measurements.

The elements I. and II. were scarcely influenced at all by having the circuit closed for half a minute; but element II. sank from 1·000 to 0·997, but quickly recovered itself completely. The following changes were caused by more prolonged closing of the circuit :—

I.

	0·998
After 10 minutes ...	0·991
„ 35 „ ...	0·988
„ 14½ hours	0·975
......	0·996
„ 15 „	0·986
5 minutes open	0·994

II.

	1·000
After 1 hour	0·994
„ 15 hours	0·988
„ 20 „	0·988
......	0·993
„ 15½ „	0·987
„ 24 „	0·986
„ 39 „	0·987
5 minutes open	0·994

III.

	1·000
After 15 minutes	0·996
„ 50 „	0·994
„ 17 hours	0·989
5 minutes open	0·992

After the lapse of a quarter of an hour the open element had in all cases recovered its former electromotive force.

* Kittler, *Sitzungsb.* loc. cit. p. 501.

The dry Daniell elements have therefore this in common with Latimer-Clark's element, that they can be prepared once for all; but they have further this advantage, that they are scarcely at all influenced by temperature; and that an accidental closing of the circuit produces only an insignificant decrease even in elements of small size (about 1 per cent.), which is very soon recovered. If the electromotive force of a Daniell element put together with copper, zinc, concentrated copper-sulphate solution, and concentrated zinc-sulphate solution be taken as 1·059 volt, then the mean electromotive force of a dry Daniell element = 1·056. It must, however, be remembered that the value 1·059 is based upon the assumption that the force of a Latimer-Clark element = 1·457 volt, which estimate is only to be considered as a preliminary one.

The resistance of element I. was 14,600 ohms, of element II. 13,500 ohms. The strength of current passing through a short-circuited element is therefore 0·000072 ampere for element II., and 0·000078 ampere for element III.; *i. e.* in the first 0·08 milligrm. copper would be deposited in the hour, and with the latter 0·09 millgrm. copper.

The dry Daniell elements are to be recommended for another purpose, viz. for charging a quadrant-galvanometer. Zamboni's pile has not proved successful for this purpose; it acts excellently for a time, but then the potential difference of its poles changes suddenly, especially with irregular changes of temperature. Apparently the deposition of moisture on the inside of the glass tube containing the pile produces a partial short-circuiting of the pile. With a water-battery these sudden changes do not occur, but the difference of potentials decreases gradually, if slowly. Errors in measurement cannot be caused thus; but the deflections of the electrometer become smaller and smaller, and, apart from the necessity of renewing the evaporated water from time to time, the whole battery every now and then has to be disconnected and cleaned from deposits of oxide and carbonate. I found the electromotive force of a newly prepared zinc and copper element filled with spring-water to be 0·992 volt. After twelve hours, during which the element remained open, it had sunk to 0·934 volt. Three of the elements forming my water-battery, which has stood now more than a year, were examined. They showed the following differences of potential :—

0·838   0·678   0·724 volt. ...... Mean 0·743 volt.

The dry Daniell elements may conveniently be combined

into a battery which requires no filling, and upon which temperature and moisture are without influence.

Since the resistance of the elements is a matter of indifference, they may be made very small. I have filled glass tubes, 8 centim. long and 5 millim. diameter, half with the copper-sulphate plaster and half with the zinc-sulphate plaster, wires of copper and zinc being placed in the corresponding mixture, which wires were then soldered together, as shown in the accompanying figure. The ends of the tubes are closed with paraffin.

Twelve such elements form a row. Twelve such rows stand one behind the other, each connected with the preceding one by insulated binding-screws, so that each chain of twelve elements hangs between two binding-screws. Any desired number of such series of twelve elements may therefore be taken to produce the charge. The whole battery of 144 elements shows a polar difference of potential

of 152 volts; whereas the same difference requires 156 elements of the freshly prepared water-battery and 200 of the enfeebled one. The whole dry battery covers a surface of 16 centim. square.
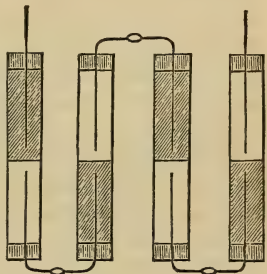
POSTSCRIPT.—In the elements last prepared the zinc wires are amalgamated at the ends and covered elsewhere with shellac, and the concentrated solutions have been diluted with one third of water.

XXIV. *The Molecular Volumes of Salt-Solutions.*—Part II. *Water of Crystallization. By* W. W. J. NICOL, *M.A., B.Sc., F.R.S.E., F.C.S., Lecturer on Chemistry, Mason College, Birmingham*[*].

IN my previous paper[†] on this subject I showed that the molecular volumes in solution of the metals sodium and potassium, and those of certain acid-radicals—Cl, (SO_4), (NO_3), (ClO_3), and (OH)—are constant in whatever way these may be combined together to form salts, the essential point to be observed being that the solutions are sufficiently

---

dilute (less than one equivalent of salt to 100 molecules of water) and of the same strength. The cause of any slight variation in the constants was shown to lie in the concentration of the solution : this must be such that the molecules of salt are without an appreciable influence upon one another; for the molecular volume of all salts increases with the concentration of the solution, but more rapidly the less soluble the salt (*loc. cit.*).

I purpose in the following pages to endeavour to prove that the conclusions arrived at in my previous paper hold good for all elements or groups of elements. I had hopes of being able to employ for this purpose the numerous determinations of the density of various salt-solutions to be found in the papers of Kremers, Schiff, Gerlach, and others, but soon found that these were of little value for my purpose, for without interpolation it is seldom possible to obtain the density of solutions of the same strength ; even where it is so, the determinations were made at different temperatures, or the density referred to water at different temperatures as unity. Only in a few cases can these old results be employed without involving considerable calculation, leading to figures which are in too many instances evidently erroneous. However, I have arranged in Table I. the apparent molecular volumes $\left(\dfrac{r}{n}\right)$ of some of the more important chlorides, bromides, and iodides, calculated by means of the following formulæ from the results of former investigators.

Where the quantity of salt is expressed in percentage,

$$\frac{r}{1} = \frac{\left[\dfrac{\left(\dfrac{Ps \times 100}{Pw} + 100\right)}{\delta} - 100\right] \times \text{M.W.}}{\dfrac{Ps \times 100}{Pw}}.$$

When in parts per 100 of water,

$$\frac{r}{1} = \frac{\left(\dfrac{P + 100}{\delta} - 100\right) \times \text{M.W.}}{P}.$$

Ps = per cent. of salt,   Pw = per cent. of water,
  δ = density,   M.W. = mol. wt. in grams.
P = parts per 100 of water.

TABLE I.

M.	MI.	MBr.	MCl.	(I—Br)M.	(Br—Cl)M.
Li	36·6	27·9	19·2	8·7	8·7
K	45·4	36·3	27·4	9·1	8·9
Na	......	25·6	17·4	......	8·2
Ca	54·2	37·7	20·2	8·5	8·7
Sr	57·7	40·1	23·5	8·8	8·3

The agreement is not very good, and in many cases the molecular volumes differ considerably from those given by me in a subsequent part of this paper; still they point to an agreement, which is not complete for the reasons given above.

After I commenced this subject, I was much struck by the fact that water of crystallization has no effect on the molecular volume of a salt in solution. The case in which I first noticed it was that of sodium sulphate, which crystallizes with ten molecules of water.

Now, if we determine the molecular volume of a solution which contains two molecules of sodium chloride (an anhydrous salt in the solid state) in the 100 molecules of water, and the molecular volume of a solution containing one molecule (2 equivalents) of sodium sulphate, we find the following:—

$$\text{Mol. vol. } Na_2Cl_2 \; 100\,H_2O = 1836\cdot3$$

$$\text{,, ,, } \quad Na_2SO_4 \, 100\,H_2O = 1819\cdot3$$

$$(Cl_2 - SO_4), \text{ then, } = \quad 17\cdot0$$

and therefore the change in molecular volume produced by the replacement of Cl by $\dfrac{SO_4}{2}$ in combination with sodium, *i. e.*

$$Na\!\left(Cl - \frac{SO_4}{2}\right) = 8\cdot5 = \Delta\,;$$

for a solution of half the strength,

$$Na\!\left(Cl - \frac{SO_4}{2}\right) = 9\cdot2 = \Delta.$$

In the case of the similar salts of potassium,

$$\text{Mol. vol. } K_2Cl_2 \, 100 \, H_2O = 1857 \cdot 1$$
$$\text{,, \quad ,, } \quad K_2SO_4 \, 100 \, H_2O = \underline{1840 \cdot 1}$$
$$(Cl_2 - SO_4), \text{ then, } = \overline{\quad 17 \cdot 0}$$

and

$$K\left(Cl - \frac{SO_4}{2}\right) = 8 \cdot 5 = \Delta,$$

as before; in a solution half the strength,

$$K\left(Cl - \frac{SO_4}{2}\right) = 8 \cdot 9 = \Delta.$$

So that the difference in Δ for solutions of the same strength is *nil* in the one case and ·3 in the other—a difference of $\frac{1}{6000}$, easily produced by the different solubilities (see *loc. cit.*, where this point is discussed).

But in the case of the sodium salts an anhydrous one is compared with a hydrated, while in the case of potassium neither salt crystallizes with water. It thus appears that water of crystallization has the same volume as water of solution. Further evidence is given by the following:—

$$(K - Na)\frac{SO_4}{2} \quad \Delta = 10 \cdot 39 ;$$

while

$$(K - Na)Cl \quad \Delta = 10 \cdot 15, .$$
$$(K - Na)NO_3 \quad \Delta = 10 \cdot 36,$$
$$(K - Na)OH \quad \Delta = 10 \cdot 06,$$
$$(K - Na)ClO_3 \quad \Delta = 10 \cdot 56.$$

This result, that the presence or absence of water of crystallization does not affect the molecular volume in solution, appeared to me most striking and well worthy of further investigation. I have therefore noted the number of molecules of water of crystallization in the salts compared in the following pages, and it will be found that the above statement is correct.

The evidence I have to bring forward in support of my previous statement with regard to the constancy of molecular or rather atomic volume exhibited by all elements and groups of elements, consists of density determinations of nearly 50 salts, representatives of all the important classes from monatomic up to triatomic acids. My former determinations are here included, either as they stand or added into the means. The results are given in one table, as before, for convenience of reference, and subsidiary tables are formed from it as occasion requires (Table II.).

TABLE II.

No.	Salt.	n.	Q.	δ.	M.W.	Aq.
1.	KCl	1	100	1·02568	1827·7	0
2.	KNO$_3$.............	2	100	1·06524	1879·6	0
3.	KHO	2	100	1·05325	1815·5	5(?)
4.	KClO$_3$	1	100	1·04122	1846·5	0
5.	K$_2$SO$_4$	·5	100	1·03758	1818·8	0
6.	KC$_2$H$_3$O$_2$	5	100	1·11077	2062·1	0
7.	,, ...	2	100	1·04932	1902·4	,,
8.	,, ...	1	100	1·02553	1850·8	,,
9.	KBr	1	100	1·04580	1835·1	0
10.	K$_2$C$_2$O$_4$	1	300	1·02205	5446·1	
11.	K$_2$CO$_3$	1	200	1·03311	3618·4	2 or 1½
12.	K$_2$C$_4$H$_4$O$_6$	1	200	1·03958	3680·5	
13.	KH$_2$PO$_4$.........	1	300	1·01727	5442·2	0
14.	KNaC$_4$H$_4$O$_6$ ...	1	200	1·03784	3671·2	
15.	NaCl	1	100	1·02255	1817·5	0
16.	NaNO$_3$	2	100	1·05980	1858·6	0
17.	NaHO	2	100	1·04712	1795·4	3½(?)
18.	NaClO$_3$	1	100	1·03844	1835·9	2
19.	Na$_2$SO$_4$	·5	100	1·03466	1808·3	10
20.	NaC$_2$H$_3$O$_2$......	5	100	1·09866	2011·5	3
21.	,, ...	2	100	1·04380	1881·6	,,
22.	,, ...	1	100	1·02280	1840·1	,,
23.	NaBr	1	100	1·04284	1824·8	2
24.	Na$_2$C$_2$O$_4$	1	400	1·01507	7225·1	
25.	Na$_2$CO$_3$	1	200	1·03038	3597·6	10
26.	Na$_2$C$_4$H$_4$O$_6$ ...	1	200	1·03664	3659·9	
27.	NaHC$_4$H$_4$O$_6$ ...	1	200	1·02755	3670·9	
28.	NaH$_2$PO$_4$	1	300	1·01636	5431·2	4
29.	Na$_2$HPO$_4$	1	200	1·03692	3608·8	12
30.	Na$_4$P$_2$O$_7$........	1	401	1·03492	7231·5	10
31.	NaPO$_3$	1	301	1·01451	5441·1	?
32.	HCl	2	100	1·01926	1837·6	
33.	H$_2$SO$_4$	1	100	1·03442	1834·9	
34.	H$_2$C$_2$O$_4$	1	200	1·01159	3647·7	2
35.	H$_2$C$_4$H$_4$O$_6$......	1	200	1·01839	3682·6	0
36.	H$_3$C$_6$H$_5$O$_7$......	1	300	1·01440	5512·6	
37.	BaCl$_2$............	1	200	1·05005	3626·5	2
38.	SrCl$_2$	1	200	1·03776	3621·7	6(?)
39.	CdCl$_2$............	1	200	1·04276	3627·8	2
40.	NiCl$_2$	1	200	1·03560	3611·1	6
41.	CoCl$_2$	1	200	1·03219	3613·4	6
42.	CuCl$_2$............	1	200	1·03347	3613·6	2
43.	LiCl	1	100	1·01353	1817·9	1 and 2
44.	Ba(NO$_3$)$_2$	1	200	1·05768	3650·4	0
45.	Sr(NO$_3$)$_2$	1	200	1·04598	3643·9	4
46.	CdSO$_4$	1	200	1·05482	3610·1	8⁄3
47.	Li$_2$SO$_4$	·5	100	1·02615	1808·1	1
48.	NiSO$_4$	1	200	1·04428	3595·5	1–6
49.	CoSO$_4$	1	207	1·04303	3720·6	1–6
50.	CuSO$_4$	1	200	1·04391	3601·4	1–4
51.	KCl	2	100	1·04959	1857·1	0
52.	NaCl	2	100	1·04393	1836·3	0
53.	K$_2$SO$_4$	1	100	1·07288	1840·1	
54.	Na$_2$SO$_4$	1	100	1·06744	1819·3	
55.	KHSO$_4$	1	100	1·05151	1841·3	
56.	NaHSO$_4$	1	100	1·04886	1830·6	

Q = number of molecules of water in the solution.

Now, treating these results as the former ones were treated, we find that the replacement of potassium by sodium in its salts produces a diminution in volume, as shown in Table III.

TABLE III.

No. in Table II.	Rad.	n.	n(K Rad.).	n(Na Rad.).	Diff.	$\Delta = \dfrac{\text{Diff.}}{n}$.	Aq.
1–15.	Cl	1	1827·7	1817·5	10·2	10·2	0–0
2–16.	NO_3	2	1879·6	1858·6	21·0	10·5	0–0
3–17.	OH	2	1815·5	1795·4	20·1	10·1	5–3½
4–18.	ClO_3	1	1846·5	1835·9	10·6	10·6	0–2
5–19.	$\dfrac{SO_4}{2}$	1	1818·8	1808·3	10·5	10·5	0–10
6–20.	$\bar{A}$	5	2062·1	2011·5	50·6	10·1	0–3
7–21.	,,	2	1902·4	1881·6	20·8	10·4	
8–22.	,,	1	1850·8	1840·1	10·7	10·7	
9–23.	Br	1	1835·1	1824·8	10·3	10·3	0–2
10–24.	$\dfrac{\bar{O}}{2}$	2	7246·1	7225·1	21·0	10·5	
11–25.	$\dfrac{CO_3}{2}$	2	3618·4	3597·6	20·8	10·4	1½–10
12–26.	$\dfrac{\bar{T}}{2}$	2	3680·5	3659·9	20·6	10·3	
13–27.	H_2PO_4	1	5442·2	5431·2	11·0	11·0	0–4
				Mean ...		$\Delta = 10\cdot4$	

In 13 cases, including 11 different pairs of salts, the mean value of $(K-Na)R$ is 10·4, the extreme variations being $-\cdot3$ and $+\cdot6$, or, omitting H_2PO_4, as the sodium salt was not quite pure, we have $\Delta = 10\cdot4 \pm \cdot3$, a difference readily produced by the different solubility of the various salts. For, as has been shown[*], this has a marked influence, owing to the attraction of the salt-molecules for one another. In order to avoid this source of error, it would be necessary to work with much more dilute solutions, in which case the experimental errors would be increased; as it is, I believe that I am fully justified in neglecting this difference and in speaking of the value of Δ in sufficiently dilute solutions as a constant: thus my former results are fully borne out.

A glance at the last column of Table III. will show that

* Phil. Mag. August 1883.

the Δ is independent entirely of the quantity of water of crystallization in the salts, the utmost variety existing in this respect failing to make itself evident in the molecular volumes.

Table IV. gives the change in molecular volume produced by the substitution of chlorine for the group (NO_3), and for bromine also the difference $M\left(NO_3 - \dfrac{CO_3}{2}\right)$.

TABLE IV.

No. in Table II.	M.	n.	$n(MNO_3)$.	$n(MCl)$.	Diff.	$\Delta = \dfrac{\text{Diff.}}{n}$.	Aq.
2–51.	K	2	1879·6	1857·1	22·5	11·3	0–0
16–52.	Na	2	1858·6	1836·3	22·3	11·2	0–0
44–37.	$\dfrac{Ba}{2}$	2	3650·4	3626·5	23·9	11·9	0–2
45–38.	$\dfrac{Sr}{2}$	2	3643·9	3621·7	22·2	11·1	0–6
			$n(MBr)$.	$n(MCl)$.			
9– 1.	K	1	1835·1	1827·7	......	7·4	0–0
23–15.	Na	1	1824·8	1817·5	......	7·3	2–0
			$n(MNO_3)$.	$n(M\dfrac{CO_3}{2})$.			
2–11.	K	2	1879·6	3618·4	61·2	30·6	0–1½
16–25.	Na	2	1858·6	3597·6	61·0	30·5	0–10

In all these cases the agreement is satisfactory, the only marked deviation being in $\dfrac{Ba}{2}(NO_3 - Cl)$; but it must be remembered that $Ba(NO_3)_2$ is an exceedingly insoluble salt, and the solution in the table is nearly saturated, while the $BaCl_2$ solution is not nearly so.

We come now to the important class of sulphates, of which seven are included in Table II.; and, as before, I have taken the difference $M\left(Cl - \dfrac{SO_4}{2}\right)$. Table V., which contains the figures for the above is divided into two parts : the first portion contains those sulphates which either crystallize with

water of crystallization or are anhydrous ; the second those
which contain water of constitution as well as water of crys-
tallization.   It is to be noted that those in the former part
of the table agree pretty closely, even though the quantities
of water of crystallization are so very different, and that those
in the latter part also agree among themselves, but the value
of Δ is about 3 units lower.

TABLE V.

No. in Table II.	M.	n.	$n(MCl)$.	$n(M\frac{SO_4}{2})$.	Diff.	$\Delta = \frac{\text{Diff.}}{n}$.	Aq.
1– 5.	K	1	1827·7	1818·8	8·9	8·9	0–0
15–19.	Na	1	1817·5	1808·3	9·2	9·2	0–10
39–46.	$\frac{Cd}{2}$	2	3627·8	3610·1	17·7	8·9	2–$\frac{8}{3}$
43–47.	Li	1	1817·9	1808·1	9·8	9·8	1–1
						9·2	
			Magnesian Sulphates.				
42–50.	$\frac{Cu}{2}$	2	3613·6	3601·4	12·2	6·1	2–5
41–49.	$\frac{Co}{2}$	2	3613·4	3600·6	12·8	6·4	6–7
40–48.	$\frac{Ni}{2}$	2	3611·1	3595·5	15·6	7·8	6–7
						6·8	

Now we have seen that water of crystallization does not
affect the molecular volume to an extent that can be recog-
nized by experiment ; the cause of this difference in the case
of the magnesian sulphates must therefore lie, not in the 6 or
4 molecules of water of crystallization, but in the single
molecule of water of constitution.   From the above experi-
ments it therefore appears probable that water of constitution
can be recognized when the salt is dissolved ; I say probable,
for owing to the difficulty experienced in preparing solutions
of these hydrated salts of the exact composition required,
some of them parting with their last molecule of water at a
temperature little below that at which the salt begins to
decompose, the results are not so concordant as in the case of
the other salts.

There is, however, another method by which this point can
be examined, and one which is totally independent of the
molecular composition of the solutions employed ; it is that
of determining the volume-change on double decomposition.

If two reactions take place, each with the formation of a definite quantity of barium sulphate and the simultaneous conversion of a corresponding quantity of a sulphate into a chloride, the volume-change should be the same in each case ; for, as I have shown above, the volume of the metal or the acid-radical is the same within narrow limits in whatever way they are combined. If, however, one of the sulphates involves water of constitution, and the other not, then, if the results in Table V. are correct, we should expect to find a difference in the volume-change.

I had considerable difficulty in devising a form of apparatus by means of which this volume-change, on precipitation, could be measured ; after numerous trials I adopted the form given in fig. 1, and afterwards that in fig. 2.

The apparatus shown in fig. 1 consists of two tubes, A and B. A has a capacity of about 50 cubic centim., B about 35 cubic

Fig. 1.
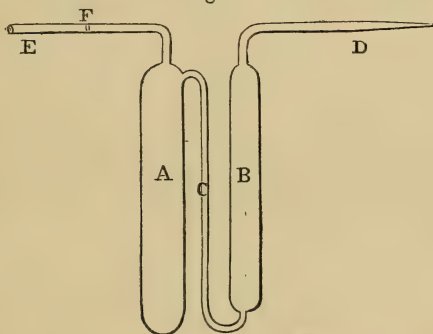
centim. They are connected by a capillary C, as shown, and the upper ends have capillaries as in a Sprengel tube. In making an experiment the apparatus is inverted, and some of the sulphate solution is sucked into B through D—the quantity to be used has been previously measured from a burette (25 cubic centim.) ; the tube is restored to its upright position, and D is dried and the whole exactly weighed : then a measured quantity (18 to 20 cubic centim.) of a solution of barium chloride of known strength is sucked into A through E, the air passing through C and up through the contents of B ; the tube must be inclined so that the solution passes down the side of A opposite to C. The apparatus is again exactly weighed. The difference in weight gives the quantity of $BaCl_2\,200\,H_2O$ experimented with. E is then washed with a little water which passes into A, and then paraffin-oil saturated with water and of known density is sucked in by E till

the whole apparatus is filled. It is then placed in the constant-temperature bath, and after some time (30 minutes) the paraffin is drawn off to mark F, as in other cases. After drying and cooling the whole is weighed; this gives the total weight before mixture. Then by suction at E the contents of B are transferred in great measure to A, and mixture is effected by shaking. The apparatus is then again filled up with paraffin; brought to a constant temperature, dried and weighed = total weight after mixture. The difference between the last two weights gives the volume-change in grams of paraffin of a known density. In this way the volume-change on mixture of even dilute solutions can be determined with considerable exactness.

Latterly I employed the apparatus shown in fig. 2, which is

Fig. 2.
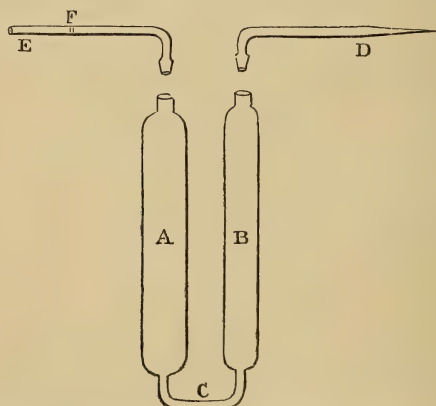
more easily used, but requires the aid of a professional glass-blower in its construction. It, too, consists of two tubes, A and B, which are joined by the capillary C. E and D are capillaries ground into A and B respectively. The bend C is filled with mercury, the liquid in excess introduced into B, and the whole weighed. The other liquid is placed in A and it is again weighed; A and B are then filled up with paraffin, and the capillary stoppers inserted, not to be moved till the experiment is completed. The remainder of the operation is the same as before, mixture being effected by drawing the liquids backwards and forwards through C. Rather better results were obtained with this form of apparatus, owing to the possible slight loss on inversion being avoided.

The advantage of the above method of experiment lies in the fact that only one solution of exact composition is required; and if this be employed for all the determinations, any error in

it is without influence on the results. Care must, however, be taken to employ an excess of the other solution; but as no appreciable effect is produced by even as much as 6 or 8 cubic centim. of excess, there is no difficulty in this.

Table VI. gives the results thus obtained. From it, it is evident the precipitation of one molecule of $BaSO_4$ is attended by the same volume-change so long as the precipitation is effected by a sulphate which contains *no* water of constitution, though it may or may not contain water of crystallization. When, however, the sulphate contains water of constitution, then there is less expansion, and the diminution is comparable with that observed in Table V. Now adding together the

TABLE VI.

A.	B.	Expansion.	Difference.	Remarks.
$BaCl_2$.	Na_2SO_4	43·5	} 43·7	Mean of 2.
,,	K_2SO_4	43·9		3 concordant.
,,	$CuSO_4$	37·7	−6·0	Mean of 2.
,,	$ZnSO_4$	37·8	−5·9	,, ,, 2.
,,	$NiSO_4$	37·2	−6·5	,, ,, 2.
,,	$MnSO_4$	38·6	−5·1	,, ,, 2.
Difference = 43·7 − expansion of $CuSO_4$ &c.				

mean difference in this Table (5·9) and that obtained in Table V. (6·8) we get 6·35; which is as close an approximation as I can make at present to the difference in molecular volume produced by a molecule of water of constitution. It is to be noted that this is a + quantity; and if the molecular volume of water of solution be 18, then that of water of constitution is 24·4.

The accuracy of the experiments on the volume-change by the precipitation of $BaSO_4$ can be shown by the following calculation:—

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$
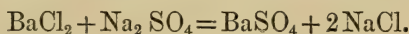
By Table II.:—

Mol. vol. of $BaCl_2$ . . . 3626·5
,,   ,, Na_2SO_4 . . . 3616·6
_____
7243·1

Mol. vol. of $BaSO_4$ . . . 51·8
,,   ,, $2NaCl + 5400$. 7236·3
_____
7288·1
7243·1
_____
Difference . . $= +$ 45·0

Again:—

$$BaCl_2 + K_2SO_4 = BaSO_4 + 2KCl.$$

Mol. vol. of $BaCl_2$	.	.	.	3626·5
,, ,, K_2SO_4	.	.	.	3637·6

                                    7264·1

Mol. vol. of $BaSO_4$	.	.	.	51·8
,, ,, $2KCl + 5400$	.	7257·1

                                    7308·9
                                    7264·1

Difference . . = 44·8

The value found by experiment was 43·7; just one unit lower, due to the contraction produced by the dilution of the $2NaCl$ or $2KCl$ solution by the 3600 water set free in the reaction. The density of $BaSO_4$ (solid) was taken as 4·5.

The above proves most clearly the accuracy of the values given in Table II., and the justice of my statement that the volumes of the metals and acid radicals are independent of the mode of combination. It also appears from the preceding Tables that the volume occupied by a metal, for instance, is the same whether it be combined with a monatomic or diatomic acid radical. The cause of this may be that in a solution there are aggregations of two or more molecules[*]; but I must reserve this point for future discussion.

Further evidence in support of the constancy of the molecular or atomic volume is to be found in the results of experiments by Ostwald[†], on the volume-change on neutralization of certain acids, organic and inorganic, by potash, soda, and ammonia. He found the difference in volume-change between KHO and $NaHO$, and between $Na\bar{H}O$ and NH_4HO, remained a practically constant number. His results are given in Table VII., along with the values I have found for some of the same reactions. Now since I have shown above that the difference $(K - Na)R$ is constant for H_2SO_4, HCl, and HNO_3, it follows that this also holds good for all the salts examined by Ostwald, and that the molecular volumes of the salt-radicals are also constant.

---

[*] Meyer, *Die modernen Theorien der Chemie*, 5th edit. p. 321 &c.
[†] Meyer, *loc. cit.* p. 453; and Ostwald, *Journ. f. prakt. Chemie*, 1877, &c.

TABLE VII.

Acid.	KHO.	K—Na.	NaHO.	Na—Am.	NH$_4$HO.
$\frac{H_2SO_4}{2}$	+11·90	0·28	......	......	−14·35
	11·5	......	11·6		
HNO$_3$	20·05	·28	19·77	26·21	− 6·44
HI	19·80	·26	19·54	25·28	6·44
HBr	19·63	·29	19·34	25·90	6·56
HCl	19·52	·28	19·24	25·81	6·57
	19·8		19·32		
HC$_2$Cl$_3$O$_2$	17·36	·29	17·07	25·73	8·66
HC$_2$Cl$_2$HO$_2$	12·95	·25	12·70	25·67	12·97
HCOOH	12·36	·21	12·15	25·74	13·59
HC$_2$ClH$_2$O$_2$	10·85	·23	10·63	25·72	15·09
CH$_2$OH.COOH ...	9·62	·10	9·52	26·01	16·49
CH$_3$COOH	9·52	·23	9·29	25·55	16·26
CH$_3$CH(OH)COOH	8·27	·14	8·13	25·87	17·74
CH$_3$CH$_2$COOH ...	7·83	·15	7·68	25·50	17·82
CH$_3$CH$_2$CH$_2$COOH	6·98	·14	6·84	25·47	18·63
CH(CH$_3$)$_2$COOH...	6·30	·13	6·17	25·44	19·27
	Mean ...	0·21	Mean ...	25·75	

Closely connected with this is the constancy observed in the thermal change attending the formation of various salts in solution from their elements, which is found to be " the sum of two constants, one dependent only on the nature of the metal, the other only on the negative constituents "[*].

Returning to Table II., we can find from it the values of $(H-Na)R$ and $(H-K)R$, and from them gain some further

TABLE VIII.

No. in Table II.	Acid.	Mol. vol. of acid.	$n(K)$.	Mol. vol. of $n(K)R$.	Differ-ence.	$\Delta(H-K) = \dfrac{\text{diff.}}{n}$.
35–12	H$_2$C$_4$H$_4$O$_6$	3682·6	2	3680·5	− 2·1	− 1·1
34–10	H$_2$C$_2$O$_4$	3647·7	2	5446·1	− 1·6	− ·8
32–51	H$_2$Cl$_2$	1837·6	2	1857·1	+19·5	+ 9·7
33–55	H$_2$SO$_4$	1834·9	1	1841·3	+ 6·4	+ 6·4
33–53	,,	1834·9	2	1840·1	+ 5·2	+ 2·6
			$n(Na)$.			$\Delta(H-Na)$.
35–27	H$_2$C$_4$H$_4$O$_6$	3682·6	1	3670·9	−11·7	−11·7
35–26	.... ..	3682·6	2	3659·9	−22·7	−11·3
24–10	H$_2$C$_2$O$_4$	3647·7	2	7225·1	−22·6	−11·3
32–52	H$_2$Cl$_2$	1837·6	2	1836·3	− 1·3	− ·6
33–56	H$_2$SO$_4$	1834·9	1	1830·6	− 4·3	− 4·3
33–54	,,	1834·9	2	1819·3	−15·6	− 7·8

[*] L. Meyer, *Die modernen Theorien der Chemie*, 5th edit. pp. 448 &c.

knowledge of the constitution of solutions; that is, we find that so long as the acid is a solid crystalline substance, the value $(H-K)=1$ and $(H-Na)=11\cdot3$. But when we have to do with a liquid or gaseous acid this constancy of difference disappears; it reappears, however, when we contrast the volume of the acid salt with that of the normal.

$$KHSO_4 \quad . \quad . \quad . \quad . \quad =1841\cdot3$$
$$K_2SO_4 \quad . \quad . \quad . \quad . \quad =1840\cdot1$$
$$(H-K) \quad . \quad . \quad . \quad . \quad =-\ 1\cdot2$$

or

$$NaHSO_4 \quad . \quad . \quad . \quad . \quad 1830\cdot6$$
$$Na_2SO_4 \quad . \quad . \quad . \quad . \quad 1819\cdot3$$
$$(H-Na) \quad . \quad . \quad . \quad = \quad 11\cdot3$$

Thus it is seen that the replacement of the first H in H_2SO_4 by $K=6\cdot4$ or $Na=-4\cdot3$, while that of the second by $K=-1\cdot2$ and by $Na=11\cdot3$, owing to the change of character of the sulphuric acid from a liquid dissolved in water to a solid body dissolved. Where the acid is solid no such difference between the first and second atoms of hydrogen is to be detected, if we except the difference $11\cdot7$, $11\cdot0$ in the case of the first and second hydrogen atoms in tartaric acid; a difference corresponding to the difference in heat of neutralization observed by Thomsen[*].

We have seen that water of constitution in solution occupies a volume greater than that of water of solution; but a comparison of the sodium phosphates in Table II. shows that the *elements* of water in a molecule occupy less volume than water. Thus:—

$$NaPO_3\,301\,H_2O \quad . \quad . \quad . \quad =5441\cdot1$$
$$NaH_2PO_4\,300\,H_2O \quad . \quad . \quad =5431\cdot2$$
$$- \quad 9\cdot9$$

and

$$Na_4P_2O_7\,401\,H_2O \quad . \quad . \quad . \quad =7231\cdot5$$
$$2(Na_2HPO_4)\,400\,H_2O \quad . \quad . \quad =7217\cdot6$$
$$- \quad 13\cdot9$$

according to whether the elements of water are contained in one molecule or in two.

To return to water of constitution and crystallization.

* *Thermoch. Untersuch.* vol. i. pp. 279 &c.

Thorpe and Watts* have shown that the volume of water of constitution in the solid state is less than the volume of the water of crystallization ; so that were the water of crystallization attached to the salt in solution, we should expect to find a very considerable increase of the molecular volume in solution ; but such is not the case. It is with very great hesitation that I venture to suggest that this is a proof that water of crystallization does not exist in solution ; there is really no evidence that is conclusive as showing the opposite. At first sight the experiments of Thomsen† and others, on the heat of hydration of various salts, lend much support to the view that water of crystallization does exist, as such, in a solution ; for there is no doubt that while in very many cases a hydrated salt dissolves in water with absorption of heat, the same salt when dehydrated evolves heat on solution. But is it not possible that the act of solution of a dehydrated salt consists, first, in the taking up of water to form a hydrate ; and that this hydrate, in dissolving, parts with its water, which thus becomes indistinguishable from the rest of the water ? When a solution, on the other hand, is concentrated, a point is reached at which the salt is capable of carrying with it a certain number of water-molecules, and *then* combination takes place. Some support of this view is to be found in the fact that it is only hydrated salts that are capable of forming well-defined supersaturated solutions, and it is only on the supposition that the molecules of water are not united to the salt that the existence and density of such solutions can be explained.

The experiments of Wüllner ‡ on the tensions of salt solutions led him to the conclusion that in some cases the water of crystallization is attached to the salt in solution, in other cases that it is not ; while Rüdorff § and De Coppet‖ have come to conclusions differing from those of Wüllner, but not agreeing among themselves.

At this point I must leave this interesting question ; but I am not without hopes of being able to solve it by experiments on the vapour-pressures of water from salt-solutions, which I have already commenced.

* Chem. Soc. Journal, 1880.
† *Thermoch. Untersuch.* vol. iii.
‡ Pogg. *Ann.* vols. ciii., cv., and cx.
§ Ibid. vols. cxiv., cxvi., and cxlv.
‖ *Ann. Chim. Phys.* 1871, 1872, 1875.

XXV. *The Periodic Law, and the Occurrence of the Elements in Nature.* By THOMAS CARNELLEY, *D.Sc. (London), Professor of Chemistry in University College, Dundee*[*].

§ 1. BUT few attempts have been made to account for the present occurrence of the elements in nature, and these may be briefly summed up in the statement generally found in text-books, that some elements, such as gold, platinum, iridium, osmium, &c., always occur in the free state; others, such as mercury, silver, oxygen, nitrogen, &c., are frequently found in this condition; others, such as lead, tin, &c., rarely so; whilst elements such as fluorine, chlorine, sodium, potassium, &c., are never found but in a state of combination. And, further, that metals occur, as a rule, most commonly in the form of oxides, sulphides, carbonates, and sulphates.

§ 2. The most interesting of such attempts is that proposed by Dr. Gladstone (Phil. Mag. [5] iv. p. 379). This, however, deals rather with the *degree of distribution* of the elements in nature than with the *form in which they occur.* In the paper referred to, Dr. Gladstone divides the elements into four classes:—(1) Plentiful, (2) Common, (3) Rare, (4) Very Rare; and he shows that the *average* vapour-density of the first class is less than that of the second, and the latter less than that of the third, and this last less than that of the fourth class. From which he concludes that those elements having the least vapour-density tended to remain more towards the surface during the period of the earth's formation, whilst elements having a high vapour-density accumulated more towards the centre, and hence occur but rarely on the surface.

Mendeljeff (*Zeitschr. f. Chem.* 1869, v. p. 405) has also pointed out that all those elements which are found in greatest quantity on the earth's surface have small atomic weights. The converse of this, however, does not appear to be true; for lithium, beryllium, and boron are far from occurring in large quantities.

§ 3. The theory proposed in the present paper, on the other hand, deals rather with the *occurrence* than with the *distribution* of the elements in nature. It has for its basis the Periodic Law of the chemical elements, first enunciated by Newlands as the Law of Octaves, and subsequently and independently developed by Mendeljeff and Lothar Meyer.

The following is a Table of the Natural Classification of the Elements in the form adopted by Mendeljeff. This table is

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[*] Communicated by the Author.

TABLE of the Natural Classification of the Elements. (After Mendeljeff.)

Groups ...	Series.	I. Monads.	II. Dyads.	III. Triads.	IV. Tetrads.	V. Triads or Pentads.	VI. Dyads or Hexads.	VII. Monads or Heptads.	Group VIII.
	1.	**H**=1							
	2.	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	
	3.	**Na**=23	**Mg**=24	**Al**=27	**Si**=28	**P**=31	**S**=32	**Cl**=35·5	
	4.	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=53	Mn=55	Fe=56, Co=59, Ni=59
	5.	**Cu**=63	**Zn**=65	**Ga**=69	....	**As**=75	**Se**=79	**Br**=80	—,
	6.	Rb=85	Sr=87	Y=89	Zr=90	Nb=94	Mo=96	.....	{ Ru=104, Rh=104, Pd= 106.
	7.	**Ag**=108	**Cd**=112	**In**=113	**Sn**=118	**Sb**=120	**Te**=125	**I**=127	—,
	8.	Cs=133	Ba=137	La=139	Ce=142	Di=147	.....	.....	
	9.	.....	.....	.....	.....	**Er**=166	.....	.....	—,
	10.	.....	.....	Yb=173	....	Ta=182	W=184	.....	{ Os=193, Ir=193, Pt= 195.
	11.	**Au**=197	**Hg**=200	**Tl**=204	**Pb**=207	**Bi**=210	.....	.....	—,
	12.	.....	.....	.....	Th=234	.....	U=240	.....	—,

now so well known that any further remarks as to its arrangement are not required in the present place, except to say that in what follows it will be necessary to bear in mind three facts in connexion with the table, and which were noticed by Mendeljeff in his original paper on the Periodic Law :—

§ 4. (*a*) That though all the elements in each group are nearly related to one another, yet those elements belonging to *even* series are much more nearly related to one another than to those of *odd* series, whilst those belonging to *odd* series are much more nearly related to one another than to those of even series.

This fact is proved by many chemical relationships which will at once suggest themselves ; for instance, elements belonging to even series never, or only rarely, unite with organic radicals to form methides, ethides, &c., whereas elements of odd series do so readily. Whilst as regards physical properties I have shown (*Deut. chem. Ges. Ber.* xii. p. 1958) that, as a rule, elements belonging to even series are paramagnetic, whereas those belonging to odd series are diamagnetic.

In the table, elements of even series are printed in ordinary type and those of odd series in thick type.

§ 5. (*b*) In the case of elements of the second series from carbon to fluorine, and of the third series from sodium to silicon inclusive, the rule stated under (*a*) is frequently reversed. This fact is rendered evident by an inspection of Lothar Meyer's curve of the elements (*Mod. Theor. Chem.*), in which it is seen that when the curve reaches carbon it rises until it comes to sodium, instead of continuing to fall, and thence from sodium to silicon it falls instead of rises. Hence the curve is exceptional at this part of its course. The exceptional or reversed character of the curve at this point represents exactly what occurs with many of the other properties of the elements lying within the boundaries indicated above.

§ 6. (*c*) Elements belonging to Group VIII. are in many respects peculiar, due no doubt to their forming the connecting link between even series on the one hand and odd series on the other; so that in some cases (as in their magnetic properties) they resemble the even series, whilst in others (as in the ease with which they are reduced to the metallic state) they resemble the odd series.

It is therefore somewhat uncertain whether the elements of this group should be placed at the end of the even series or at the beginning of the odd series. This uncertainty, however, does not arise in the case of Meyer's curve; for the position of these elements on the curve makes it quite evident that they

form the gradual passage from even series to odd series, or rather from the falling to the rising portions of the curve, since the elements of this group always form the minima of the curve.

§ 7. After the above somewhat lengthy but necessary introduction, we may now proceed to the proper subject of the paper. This may be divided into three heads:—(1) the *reducibility* of the elements to the free state from their state of combination; (2) occurrence of the elements in the *free state* in nature; (3) occurrence of the elements in the *combined state* in nature.

§ 8. (1) REDUCIBILITY OF THE ELEMENTS.—*Elements belonging to* odd *series are, as a rule, easily reducible to the free state, whilst those belonging to* even *series are only reducible to the free state with difficulty.*

The only exceptions to this rule are as follows :—(*a*) C, N, O, Na, Mg, Al, and Si, for explanation of which see § 5. (*b*) The elements of Group VIII., for which see § 6.

§ 9. (2) OCCURRENCE OF THE ELEMENTS IN THE FREE STATE IN NATURE.—This is, of course, closely connected with the property of reducibility already considered, so that we may expect a similar relation to hold good. An inspection of the Table in fact shows that—

Elements belonging to even *series (except* C, N, O, *and* Group VIII.) never *occur in the free state in nature; whereas elements belonging to* odd *series generally and sometimes frequently do so occur.*

Thus the following elements of odd series are frequently found in the free state:—Cu, Ag, Au, Hg, As, Sb, Bi, S, Se, Te; whilst Pb and Sn sometimes occur native. Ga, In, Tl, and Cd are distributed so sparsely that we can scarcely say whether they occur free or not.

Of elements belonging to odd series which have not been found free, Cl, Br, I, F, Zn, and P are therefore the only notable exceptions, since Na, Mg, Al, and Si may be accounted for by § 5.

As regards the exceptions among *even* series, C, N, and O fall under § 5, and Group VIII. under § 6. It may further be said in reference to this group, that all the elements belonging to it except Co occur native; Fe and Ni, however, only in meteorites. Of the three sets of triads belonging to this group, the tendency to occur in the free state increases as the average atomic weight of each triad increases. Thus the triad Os, Ir, Pt are more likely to occur free than the triad Ru, Rh, Pd; and the latter more likely than the triad Fe, Co, Ni.

§ 10. (3) OCCURRENCE OF THE ELEMENTS IN THE COMBINED STATE IN NATURE.—In reference to what is said under this section, F, Cl, Br, I, and the elements of Group VIII. must be neglected, as they will be considered further on, §§ 11, 12.

Elements belonging to odd *series usually occur in nature as sulphides or double sulphides*, i. e. in combination with a negative element belonging to an* odd *series, and only in very few cases as oxides; whereas elements belonging to* even *series, on the other hand, usually occur as oxides or double oxides (forming silicates, carbonates, sulphates, aluminates, &c.), i. e. in combination with a negative element belonging to an* even *series, and never (with two exceptions) as sulphides.*

Thus:—

Elements belonging to Even series:—

As oxides or double oxides.
{
Commonly. Li (lithia mica, &c.) K (nitre, felspar, &c.), Rb, Cs, Be, Ca, Sr, Ba, B, Sc, Y, La, Yb, C, Ti, Zr, Ce, Th, V, Nb, Di, Ta, O, Cr, Tb, W, Mn.
Frequently. N (in nitre), Mo.
Rarely or never. None.
}

The only two of these elements occurring as sulphides are:—

{
Commonly. Mo.
Very rarely. Mn (also O, as SO_2 in volcanic gases).
}

Elements belonging to Odd series:—

As sulphides (selenides, tellurides).
{
Commonly. Cu, Ag, Zn, Cd, Hg, Ga, In, Tl, Pb, Sb, S, Se, Te.
Frequently. As, Bi, Sn.
Never. Au (occurs only in free state in nature); Na, Mg, Al, Si, P (for these see § 5).
}

As oxides......
{
Commonly. Na, Mg, Al, Si, P (for these see § 5), and Sn.
Frequently. Zn, Cu.
Rarely. Pb, Sb, Bi, As.
}

§ 11. *Group* VIII.—The elements of this group, except Fe, Co, and Ni, never occur in nature in the combined state, and therefore need not be considered in this connexion. As regards the first triad of the group,

* Also as selenides, tellurides, and arsenides.

Fe occurs *mostly* as oxide, but also *frequently* as sulphide;

Co occurs *mostly* as sulphide and arsenide, but *sometimes* as oxide;

Ni occurs *almost always* as sulphide and arsenide, and only *very rarely* as oxide.

Iron, the first member of the triad, thus more nearly resembles elements of the even series; whereas nickel, the last member, more nearly resembles elements of the odd series. This shows therefore in a marked manner that in Group VIII. we have a gradual passage from even series on the one hand to odd series on the other.

§ 12. The halogens Cl, Br, I, and F, being the most electronegative of the elements, occur in nature in combination with the most electropositive metals as chlorides, bromides, iodides, and fluorides, &c., and are never (if we omit a few metallic oxychlorides, and sulphochlorides) found in combination with either oxygen or sulphur.

§ 13. The only other point necessary to mention is that, as regards the odd members of any one group, the tendency to occur in nature as sulphides increases, whereas the tendency to occur as oxides or double oxides diminishes, as the atomic weight increases, thus :—

Group I.
{
Na^*, frequently occurs as double oxide (silicates, Chili saltpetre &c.) and never as sulphide.

Cu, occurs commonly both as sulphide (Cu_2S, CuS, $Cu Fe S_2$, &c.), and as oxide or double oxide ($Cu_2 O$, CuO, malachite, &c.).

Ag, generally as sulphide and never as oxide.

Au, only in free state.
}

Group II.
{
Mg, always occurs as double oxide ($MgCO_3$ &c.).

Zn, most commonly occurs as sulphide, but sometimes also as oxide.

Cd, only found as sulphide and never as oxide.

Hg, only found as sulphide or in metallic state, and never as oxide.
}

Group IV.
{
Si, always occurs as oxide or double oxide (silicates).

Sn, almost always occurs as oxide, but sometimes as sulphide.

Pb, almost always occurs as sulphide, and only rarely as oxide (minium).
}

And a similar thing for Groups III., V., and VI.

* Omitting its occurrence as chloride, since it does not affect the present question.

§ 14. The whole of the facts stated above under §§ 8, 9, 10, 11, 12 may be expressed in terms of Lothar Meyer's Curve of the Elements as follows :—

Elements standing on falling *portions of the curve are reducible with difficulty, and never occur in the free state in nature, or in combination as sulphides, but always in combination with oxygen, forming oxides or double oxides (silicates, sulphates, carbonates, &c.); whereas elements standing on* rising *portions of the curve are easily reducible, and almost always occur (more or less) in the free state in nature, and also in combination with sulphur, and but rarely with oxygen.*

By stating the relations in this way, almost all the exceptions mentioned in §§ 8–12 are got rid of and fall in with the rule.

This example, with numerous others which might be mentioned, shows how truly Meyer's Curve of the Elements is an exact exponent of the facts of nature.

XXVI. *Harmonic Motion in Stellar Systems. By* Professor PLINY E. CHASE, *Haverford College, Philadelphia, U. S. America*[*].

THE principle of harmonic motion is of "immense use not only in ordinary kinetics, but in the theories of sound, light, heat, &c." (Thomson and Tait, 'Nat. Phil.' i. sec. 52).

In studying kinetic correlations, we find that the most obvious and immediate control is exercised by inertia, attraction, and repulsion. In the solar and stellar systems, the principles of universal gravitation and of æthereal oscillation are simultaneously and mutually operative, in ways which are indicated, as I think, by observable relations among cosmical masses, distances, velocities, and orbital periods.

Various forms of cyclical oscillation may be represented and coordinated by the formula

$$gt^2 = \pi^2 l = \pi^2 L^3 = M = 2h.$$

In this formula, g represents gravitating acceleration on an oscillating particle ; $t =$ cyclical time of a single oscillation (or half-time of rotation or revolution); $l =$ length of linear pendulum, or radius of circular orbital revolution ; $L =$ radius of free revolution $\div$ radius of constrained nucleal rotation, as explained in the following paragraph ; $M =$ modulus, or height of homogeneous elastic atmosphere which would pro-

pagate waves with the velocity gt; $h =$ height of fall in time t, or of projection with velocity gt, or of alternate fall and rise in perpetual elastic rebound with maximum velocity gt. At Sun's surface, where g is a maximum for our system, and where the collisions of subsiding particles have changed free revolution into constrained rotation, $gt = $ *the velocity of light.* Therefore, if we designate the velocity of light by v_λ, and remember that in an expanding or contracting rotating nucleus $g \propto \dfrac{1}{r^2}$, while t varies as r^2, the modulus velocity of æthereal oscillation, of nucleal rotation, and of limiting gravitating acceleration, in the solar system has been, is, and will continue to be v_λ. Hence we derive the universal equation

$$g = \frac{v_\lambda}{t} \cdot \frac{m}{r^2} ;$$

which holds for all masses and distances, provided m and r are expressed in terms of Sun's mass and semidiameter.

Laplace (Bowditch's translation, III. vii. § 47 [2128[2]]) shows that the solar " atmosphere can extend no further than to the orbit of a planet whose periodical revolution is performed in the same time as the sun's rotatory motion about its axis." Faye (*Comptes Rendus*, April 21, 1884, p. 949) traces the indication of this limit to Kant. I designate it therefore by ρ_κ, Sun's semidiameter being ρ_0 and $L = \rho_\kappa \div \rho_0$. It may be deduced from v_λ as follows:—

Let $t_\lambda = $ time required by a luminous wave to pass from Sun to Earth; $v_0 = $ limiting velocity of planetary revolution at Sun's surface $= \sqrt{\gamma_0 \rho_0}$; $v_r = $ velocity of solar equatorial rotation. Then, if we take Nyrén's estimate of the constant of aberration (' The Observatory,' vi. p. 365),

$$t_\lambda = 20''{\cdot}492 \times 31558149^s \div 12936000'' = 498^s{\cdot}99; \ \ L^{\frac{3}{2}} = v_0 \div v_r;$$

$$\pi L^{\frac{3}{2}} = \frac{v_\lambda}{v_0}; \ \ \pi L^3 = \frac{v_\lambda}{v_r}; \ \ v_\lambda = 214{\cdot}45\,\rho_0 \div 498{\cdot}99 = {\cdot}42977\,\rho_0 ;$$

$$v_0 = 2\pi \times 214{\cdot}45^{\frac{3}{2}} \rho_0 \div 31558149 = {\cdot}000625255\,\rho_0 ;$$

$$\frac{v_\lambda}{v_0} = 687{\cdot}351 ; \ \ L = (687{\cdot}351 \div \pi)^{\frac{2}{3}} = 36{\cdot}301.$$

Bode's law, notwithstanding its failure in the case of Neptune, may perhaps be a partial expression of a more extensive and more general law. Indeed, within the solar system, planetary or belt-positions are nearly represented by the series 4, 7, 10, 16, 28, 52, 100, 196, 292, in which there are two

equal intervals at the outer limit as well as two at the inner limit, and the intermediate positions follow Bode's progression. If we determine, by the method of least squares, the law of planetary progression, we find that it is suggestive of harmonic parabolical subsidence.

Suppose Sun to be in the focus of a paraboloid of revolution, with a directrix-plane at $\dfrac{1}{3\rho_0}$ and a vertex at $\dfrac{1}{6\rho_0}$. Suppose the nearest fixed star (presumably α Centauri) to be in the axis of the same paraboloid. Take 39 numerical abscissas of the form $A_n = \xi \eta^n \zeta^{n^2}$, with $A_0 = \xi = \frac{1}{6}$, $A_{19} = \frac{4}{9}L$, $A_{38} = LM \div \rho_0 = \pi^2 L^4$. One third of the abscissas $(A_0 .. A_{12})$ are within the solar photosphere; one third $(A_{13} .. A_{25})$ are extra-solar and inter-asteroidal; one third $(A_{26} .. A_{38})$ are extra-asteroidal and inter-stellar. The next abscissa (A_{39}) is in a region of predominating stellar influence, approximately, and *perhaps* exactly, in the locus of α Centauri. The twenty-seven extra-solar and inter-stellar abscissas may also be divided into three equal suggestive groups, $A_{12} .. A_{20}$ being inter-planetary; $A_{21} .. A_{29}$ having significant planetary relations; $A_{30} .. A_{38}$ being extra-planetary. The middle group $(A_{21} .. A_{29})$ represent, respectively, $\frac{1}{2}$ Mercury, $\frac{1}{2}$ Venus, $\frac{2}{3}$ Earth, $\frac{3}{4}$ Mars, $\frac{4}{5}$ asteroid, $\frac{5}{6}$ Jupiter, $\frac{6}{7}$ Saturn, $\frac{7}{8}$ Uranus, $\frac{7}{6}$ Neptune, the indicated loci being all within orbital limits. We find here, as in the Bodeian series, two equal numerators at the outer limit, where the harmonic mean of the two coefficients is unity, as well as two at the inner limit, where the harmonic mean is $\frac{1}{2}$. The coefficients $\frac{1}{2}$, $\frac{2}{3}$, &c. represent successive and progressive harmonic rupturing tendencies, inasmuch as particles falling toward a cosmic focus from a distance nr would acquire the dissociative velocity $\sqrt{2gr}$ at $\dfrac{n}{n+1}r$. The reciprocal character of the Saturnian and Neptunian coefficients furnishes an indication of such retrograde tendencies as we may naturally look for at the outer limits of a planetary system.

Although it is impossible at present to anticipate with certainty the precise way in which undiscovered harmonic influences will be manifested, it may be possible to show the probable existence of such influences and where to look for them. The tendency to make absolute any close approximation to simple numerical relations, which is found in Jupiter's satellites, should likewise prevail in planetary motions. The number of such tendencies among the cosmical masses and positions is so great that it is difficult, for want of definite criteria, to judge of their relative importance. It may perhaps

finally be found that they are all satisfied by adjustments of orbital eccentricity.

In seeking illustrations and estimating the relative importance of the harmonic adjustments of cosmical masses, we may be guided by the following considerations :—

1. Sun (m_0) is the chief centre of nucleation.

2. Earth (m_3) is the chief centre of condensation, since it is the largest of the dense planets, and its orbit traverses the secular centre of the belt of greatest condensation.

3. Jupiter (m_5) is the chief centre of planetary nebulosity, since it is the largest planet, and its orbit traverses the centre of the planetary system when Neptune and Uranus are in opposition.

4. Saturn (m_6) is the centre of nebular planetary inertia, since $\sqrt{\Sigma m r^2 \div \Sigma m}$ is in Saturn's orbit.

The harmonic relation of solar gravitation to the velocity of light appears to have exerted a secondary influence at the chief centre of condensation, for we find

$$g_3 : g_0 + g_3 : : (v_\lambda \div g_0 = t_0) : \left(\frac{v_\lambda}{g_0} + \frac{v_\lambda}{g_3} = 1 \text{ year} \right).$$

The mass-ratio which satisfies this proportion is $m_0 = 327400 m_3$.

A combination of the harmonic influences of the chief centres of nucleation, condensation, and nebulosity seems to be shown by Earth's and Jupiter's modulus-velocities of rotation ; since $g_3 t_3 =$ circular-orbital velocity at the mean centre of gravity of $\odot$ and $\m4$, while $g_5 t_5 =$ circular orbital velocity at Sun's surface. The equation which satisfies these harmonics is $m_0 = 1054 \cdot 6 \, m_5$.

The total *vis viva* of gravitating subsidence in equal æthereal spheres, which varies as m^3, seems to have cooperated with luminous undulation in determining the ratio of the two great planetary masses, at the centres of nebulosity and of planetary inertia. The proportion $m_5^3 : m_6^3 : : \rho_\kappa : \rho_0$ gives $m_0 = 3491 \cdot 8 m_6$.

The mass of the exterior belt seems to have been mainly determined by simple oscillatory relations to the chief centre of nebulosity, and the subdivisions of the belt by *vis viva* of subsidence, as appears by the equations

$$\pi^2 (m_8 + m_7) = m_5,$$

$$\rho_8 \div \rho_7 = m_8^3 \div m_7^3,$$

which give $m_0 = 22497 \, m_7$; $m_0 = 19370 \, m_8$.

The ratio of Venus to Earth appears to be such as to give the two planets equal orbital momenta. This harmony would be satisfied by the equation $m_0 = 384962 m_3$.

The outer masses of the belt of greatest condensation are perhaps connected with the inner masses, by the same relations as exist between the outer belt of the system and the chief centre of nebulosity.

$$\pi^2(m_1 + m_4) = m_2 + m_3,$$

$$\rho_1 \div \rho_4 = m_1^3 \div m_4^3.$$

These harmonics give $m_0 = 4503361 \, m_1 = 2852190 \, m_4$.

The accordance of the foregoing harmonic values with recent astronomical estimates is shown in the following Table:—

		Harmonic.	Astronomical.	
$m_0 \div m_1$	.....	4503361	4488285	Encke.
$m_0 \div m_2$	.....	384962	394094	Hill.
$m_0 \div m_3$	.....	327400	326800	Newcomb.
$m_0 \div m_4$	.....	2852190	2853500	Hall.
$m_0 \div m_5$	.....	1054·6	1050	Leverrier.
$m_0 \div m_6$	.....	3491·8	3482	Hall.
$m_0 \div m_7$	.....	22497	$22600 + 100$	Newcomb.
$m_0 \div m_8$	.....	19370	19380 ± 70	,,

XXVII. À priori *Probabilities.*
By F. Y. Edgeworth, *Lecturer on Logic at King's College*[*].

I. A *PRIORI* probabilities not determined by statistics underlie many important calculations both in Physics and Social Science. (1) In the measurement of a physical quantity it is generally assumed that, prior to observation, one value of the quæsitum is as likely as another. Take, for example, the following[†] simple problem:—Given a set of observations in a line, x_1, x_2, x_3, diverging according to a given probability-curve from a sought point x. x is found from the equation

$$\frac{d}{dx} \rho h \frac{1}{\sqrt{\pi}} \, \epsilon^{-h^2\left\{(x-x_1)^2 + (x-x_2)^2 + \&c.\right\}} = 0,$$

where ρ is the *à priori* probability that the real value of the quæsitum is between x and $x + \Delta x$. It is generally assumed that ρ is constant. But if not, let it equal $\Delta x \chi(x)$, where Δx is an indefinitely small constant. Then the equation

$$2h^2 \times \left\{(x-x_1) + (x-x_2) + \&c.\right\} = 0$$

will have to be modified by adding to the left-hand member the term $\dfrac{\chi'(x)}{\chi(x)}$. Again, in the problem* which may be placed next to the above in point of simplicity, viz. given a set of observations diverging from a known point according to a sought modulus, it has been tacitly assumed that, *à priori*, one value of the modulus is as likely as another. But, if it is not so, let $\chi(h)\Delta h$ express the distribution of *à priori* probability. Then the equation to zero, from which the reciprocal of the modulus squared is found to be half the reciprocal of the mean square of error, will have to be modified by adding to the left-hand member the term

$$\chi'(h) \div \chi(h)h^{n-1}.$$

A fortiori in the problems compounded of those simple cases; in particular those which we distinguished in a former paper† as Probs. III. and IV. And if we ascend to the higher problems‡, which are not restricted to exponential laws of error, and to the more sublime quæsitum of utility as distinguished from probability, there also does the necessity of an *à priori* foundation confront us. *A priori* also is the basis of the important theorem which determines the probability that two sets of observations have diverged from different means.

(2) The preceding remarks relate primarily to the measurement of objective continuous quantities, real spaces and times —for instance, a star's position in the heavenly sphere, or its time of crossing the meridian. What is true of this class of measurables is true, *mutatis mutandis*, in the case of integer numbers, and of the Means which have been called subjective, fictitious, or typical. An example of a real integer number estimated by a sort of method of observation, is Jevons's§ calculation of the number of sovereigns in currency. Examples of the fictitious Mean are :—in space an average group of barometrical heights, in time the average flowering-time of a plant, in integer number all the Registrar-General's returns. We are not now concerned to examine the distinctions which have just been indicated. For the present purpose we may compare with the first problem of the preceding paragraph the statistical practice of taking the mean of a large number of figures. The analogues in integer number of the problems in continuous quantity which involve the determination of a modulus are less familiar. Statistical examples resembling

* Phil. Mag. 1883, vol. xvi. p. 366.   † Ibid.
‡ Phil. Mag. February 1884.
§ 'Investigations in Currency and Finance,' Essay IX

the problem intermediate* between our III. and IV. will be found in Hain's *Statistik des Oesterreichischen Kaiserstaates.* In so far as these methods are applications of Inverse Probabilities they involve à *priori* assumptions†. And the theorem which assigns the probability that the difference between two sets of statistics‡ (*e. g.* male and female births) is not accidental is similarly founded on an à *priori* basis.

(3) In examining the foundations of some of the problems mentioned we shall find a still lower depth of à *priori* probability. In calculating à *posteriori* the probability that two sets of observations or statistics result from different Means (whether of the real or the fictitious species), we seem to make some assumption as to the probability that the two means should be identical. And generally, in calculating à *posteriori* the probability that a certain phenomenon is not the result of chance§, we make some assumption as to the à *priori* probability that the *régime* of chance§ existed. This is pointed out by Boole and Donkin in several brilliant papers‖ which appeared in this Journal. It seems impossible to deny that, with respect to these à *priori* probabilities, the theory of Boole and Donkin is more correct than the practice of Laplace¶ and Herschel.

(4) Thus the Calculus of probabilities, as applied to the most important problems, requires à *priori* data. It may, however, be denied that those problems require the calculus for their solution. It may be plausibly maintained that the effective inference is not of the nature of Inverse Probability, but ordinary Induction. When we conclude that the ratio of male to female births is (say) 104 : 100, we need not calculate inversely the probability that the given statistics would have

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* Phil. Mag. 1883, vol. xvi.

† This remark extends of course to the so-called Law of Succession, which may be regarded as a deduction (by way of Bernouilli's theorem) from one of the inverse theorems contemplated in this paragraph. The analogue in *observations* of this descent after ascent is given at p. 374, Phil. Mag. 1883, vol. xvi.

‡ The line between "observations" and "statistics" may thus perhaps be drawn: the former is concerned with real, the latter with fictitious, Means. Or, less philosophically perhaps (transferring to "Statistics" an inquiry, like Jevons's above indicated, as to a real integer number), they are distinguished from each other, as are the subjects of our first and second paragraphs. The complaints which have been made by previous writers (Cournot, Ellis, and Mr. Venn) against Inverse Probability do not seem to have included the case of Observations in the narrower sense of the term: real Means in continuous quantity.

§ Or any other specified mode of origin.

‖ Phil. Mag. 1851.

¶ *Cf.* Phil. Mag. 4th series, vol. i. p. 462, vol. ii. p. 97.

resulted from any other mean. It suffices to infer inductively that, because groups of statistics having that ratio as mean have been in great numbers presented in the past, such groups will be reproduced in the future; then to take the Mean as the representative of the group; by the light of common sense, or according to a more formal principle to be set forth hereafter. The case of observations and statistics of different *weight* presents indeed a difficulty, but not perhaps an insuperable one, in the way of this procedure. Although the objection seems to have a good deal of force, yet it cannot reasonably be allowed to dispense altogether with the Calculus. At least in cases where our data are not indefinitely numerous we must apply a stroke of inverse probability. And even in cases more favourable to unaided induction, though without the calculus we might be confident that a discrepancy in statistics corresponded to a difference of cause (for example, in the case of male compared with female births), yet could we have an adequate conception of the *degree* of that assurance without the mathematical calculations of a Laplace? In fine, is any one competent to assert that those reasonings of the greatest intellects* should be put into the fire?

II. If, then, *à priori* probabilities are required, it behoves us to consider how far that requirement is fulfilled.

(1) It is fulfilled sufficiently to allow of a mathematical, though not a numerical, inference in cases where the *à posteriori* probability has a limiting value, provided that an involved *à priori* probability is not extreme. For example, in the first problem of our first paragraph, when n is indefinitely large, we may neglect the correction introduced, provided that $\dfrac{\chi'(x)}{\chi(x)}$ is finite; which seems to be in general reasonably certain. And similarly in the second problem, and subject to a similar proviso, the correction in comparison with the term corrected is neglectible when n is indefinitely large. The remark extends to the problem intermediate between III. and IV. It extends also to the important theorem which assigns the probability that a difference in observations or statistics corresponds to a difference in cause. This is well indicated by Cournot (with regard to statistics at least), though he hardly seems aware that his formula correcting the extent of error and the probability of its occurrence† has no *numerical* validity upon his view of *à priori* probabilities. Again, the indeter-

* See *e. g.* Laplace, *Essai Philosophique*, p. lix, 3rd edit., *Théorie Analytique*, Book II. p. 31; Herschel, 'Essays,' p. 422 (Review of Quetelet); De Morgan, *Encycl. Metropol.* §§ 145-6.
† *Exposition de la Théorie des Chances*, ch. viii.

minate constants introduced by Boole and Donkin into the
expression for *à posteriori* probabilities do not refuse a quan-
titative though not numerical conclusion ; provided that we
know something of those *à priori* probabilities : that they are
not extremely great or small*. Since, indeed, these constants
are of a somewhat *fainéant* character, and have at most a veto
on the conclusion, there seems a good deal to be said (beyond
what has been said by Boole and Donkin†) in favour of the prac-
tice of Laplace and Herschel and other high authorities, who
omit these constants in their estimate of *à posteriori* probability.
Only it must be remembered that such measures are not of
the exacter species contemplated by Herschel‡ and DeMorgan§,
but rather like economic measures of utility, not proportional
to the thing measured, but increasing with its increase and
decreasing with its decrease in general and in the absence of
extraordinary circumstances.

(2) If greater precision is desiderated, may we postulate that
the measurables in our first two paragraphs and the constants
representing probability in our third paragraph do as often
have one value as another (of all the values which they can
possibly have, or at least over a certain range of those values).
Such a postulate is based by the present writer‖ upon a sort
of unconscious induction; like that upon the strength of which
it has been believed (correctly, as more definite experience
shows) that one digit in general recurs as often as another.
This position is not exposed to Boole's remark¶ upon *à priori*
probability, which Mrs. Bryant** has lately reinforced. They
seem to fire altogether above our humble empirical ground.
But it may be well to show that, as we are not aimed at, so
neither are we hit. Boole, objecting to the assumption that
à priori one value of a probability-constant is as likely as
another, propounds a counter hypothesis according to which
à priori probabilities are no longer evenly distributed, but
crowded together in the neighbourhood of the value $\frac{1}{2}$. The
reply is†† that the hypothesis does not agree with fact, that
experience (*e. g.* the Registrar-General's returns) presents a
great variety of statistical ratios, and no decided preponder-
ance of the ratio $\frac{1}{2}$. Mrs. Bryant follows, objecting " that if
all frequencies of the event Y are equally probable, the fre-
quencies of the event which consists in a Y following a Y are

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* See Phil. Mag. 4th series, vol. i. p. 360, vol. ii. p. 99 ; *Cf.* 'Mind,'
April 1884, *the Philosophy of Chance.*
† Phil. Mag. 4th ser. vol. i. p. 462, vol. ii. p. 98.
‡ 'Essays,' p. 369.   § 'Formal Logic,' chapter on Probability.
‖ 'Mind,' April 1884 ; 'Hermathena,' May 1884.
¶ 'Laws of Thought,' p. 370.   ** Phil. Mag. June 1884.
†† *Cf.* 'Mind,' *loc. cit.*

not equally probable. The hypothesis is thus shown to be inconsistent, since it cannot be applied to these two unknown events of Y and Y repeated." Of course it must be admitted that, if a certain variable has as often one value as another, a second variable depending upon the first may not enjoy that equal distribution of values. If the stars are distributed at random over the heavenly sphere, then the distance between a star and its nearest neighbour will not have one value as often as another. Very great and small distances will be rare. If cannon-balls be fired with constant velocity from a cannon which is directed at random to any point on a sphere described about the turning-point as centre, the balls descending will not strew the earth uniformly like snow. And, to come to the point, if the probability p of an occurrence X is uniformly distributed between 0 and 1, then the probability P of the double event x, x will not be distributed uniformly, but according to this law: that the probability of the *à priori* probability being between P and P $+\Delta$P is (not ΔP) but Δp, that is in the limit ΔP $\dfrac{dp}{d\mathrm{P}}$, that is ΔP $\dfrac{1}{2\sqrt{\mathrm{P}}}$, since P $=p^2$. Which seems contrary to experience.

(3) Let it be granted, however, that Boole and his followers hit a weak point if they suggest that, though *something* in each class of phenomena occurs as often one way as another, it is not always possible to determine *what* it is which is thus equally distributed, whether our cannon is aimed indifferently in every direction, or our cannon-balls fall uniformly like snow. Still we may fall back upon the position that, where the form of a function is completely unknown, it is allowable to assume that form which is most convenient for the purpose of calculation (especially where we have reason to suppose that the results of different hypotheses are not widely different). It is upon this principle that Laplace took the first step in his celebrated method of Least Squares, assuming that the quæsitum is an arithmetic mean of the observations. If, indeed, the views put forward in a former paper in this Journal are correct, that step is by no means so precarious as has been supposed. Still that Laplace should have taken that step in the dark and that it should turn out to be correct is very instructive. The same principle must be employed in the determination* of a change in the general purchasing power of gold, and probably in many other parts of Social Science. The principle seems especially appropriate to cases where we seek, not so much an exact measurement, as

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* 'Statistical Journal,' Jan. 1884.

the order of the probability which attaches to an hypothesis. Accordingly the principle affords a foundation for Donkin's[*] elaborate calculation of the probability of a physical connexion between binary stars. However, it may be admitted that his assumption concerning the genesis of double stars, though doubtless the simplest that could be made, yet does not exceed rival assumptions in respect of simplicity and convenience to the same extent as the assumption of an arithmetic mean in the cases just referred to excels the geometric and all other means.

To sum up, there has been expressed a doubt [I. (4)] how far the area of applied Inverse Probabilities extends. But, as far as it does extend, so far, in general and with the trifling exception of games of chance [I. (1)–(3)], a foundation of unstatistical *à priori* probabilities is required. The only perfectly solid foundation of this character which exists is, as it were, a shapeless mass of rough experience [II. (1)] adequate to support an unnumerical *à posteriori* probability. To afford a basis for the more regular structures of the science that rude foundation must be levelled by the addition [II. (2)] of a somewhat less solid, but still empirical, material. And after all [II. (3)] there remain fissures to be filled up by legitimate conjecture. How much such a foundation will support, to what height it is expedient to carry an arithmetical calculation founded thereon, is a question to be determined by that unwritten philosophy and undefinable good sense which, in the order of scientific method, precedes the application of Calculus and is prior to *à priori* probabilities.

XXVIII. *On the Liquefaction of Oxygen and the Critical Volumes of Fluids.* By JAMES DEWAR, *M.A., F.R.S., Professor of Chemistry at the Royal Institution, &c.* †

HAVING had occasion to illustrate, in my lectures at the Royal Institution, the liquefaction of oxygen, a short description of the apparatus I have found most convenient for such demonstration may interest the readers of the Philosophical Magazine. The two Russian chemists MM. Wroblewski and Olzewski, who have recently made such a splendid success in the production and maintenance of low temperature, have used in their researches an enlarged form of the well-known Cailletet apparatus; but for the purposes of lecture demonstration, which necessarily involves the projection on a screen of the actions taking place, the apparatus repre-

sented in the annexed woodcut is more readily and quickly handled, and enables comparatively large quantities of liquid oxygen to be produced. The arrangements will be at once understood on looking at the figure, which is taken from a photograph. The oxygen- or air-reservoir, C, is made of iron;
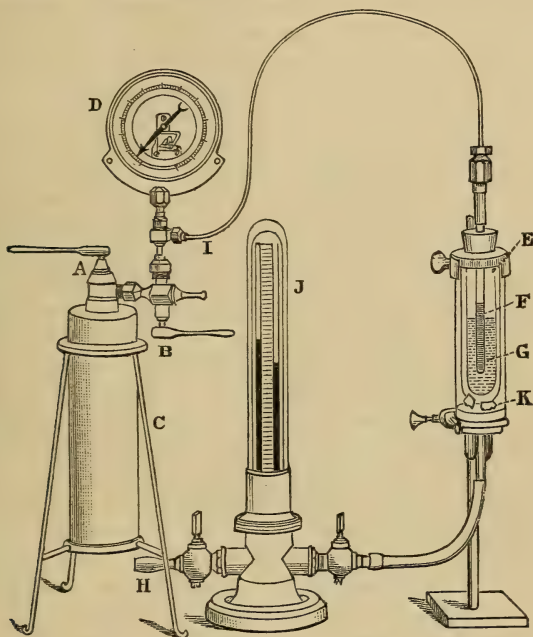
it contains gas compressed for convenience to 150 atmospheres. A is the stopcock for regulating the pressure of the gas in the glass tube F, and D is the pressure-manometer, the fine copper tube which connects the gas-reservoir and the glass tube, F, being shown at I. The air-pump gauge is marked J, the tube leading to the double oscillating Bianchi being attached at H. The glass test-tube G, which contains the liquid ethylene, solid carbonic acid, or liquid nitrous oxide, which is to be boiled *in vacuo*, is placed in the middle of a larger tube. It has holes, shown at E, in the upper part, so that the cool vapours in their course to the air-pump are forced to pass round the outside of the vessel and help to guard it from external radiation. The lower part of the outer cylinder is covered with pieces of chloride of calcium, shown at K. If a thermometer is used and a continuous supply of ethylene maintained, the india-rubber cork through which the tube F passes has two additional apertures for the purpose of inserting the

respective tubes. When the pump has reduced the pressure to 25 mm., the ethylene has a temperature of about —140° C.; a pressure of between 20 and 30 atmospheres is then sufficient to produce liquid oxygen in the tube F. The tube F is 5 mm. in diameter and about 3 mm. thick in the walls, and when filled with fluid oxygen (for projection) holds at least 1·5 cubic centim. With such a quantity of fluid oxygen it is easy to show its ebullition at ordinary pressures, and by means of a thermo-junction to demonstrate the great reduction of temperature which is attendant on its change of state at atmospheric pressure.

Provided a supply of liquid ethylene can be had, there is no difficulty in repeating all the experiments of the Russian observers ; but as this gas is troublesome to make in quantity, and cannot be bought like carbonic acid or nitrous oxide, such experiments necessitate a considerable sacrifice of time. It was therefore with considerable satisfaction that I observed the production of liquid oxygen by the use of solid carbonic acid, or preferably liquid nitrous oxide. When these substances are employed and the pressure is reduced to about 25 mm., the temperature of —115° C. may be taken as that of the carbonic acid, and —125° C. as that of the nitrous oxide. As the critical point of oxygen, according to the Russian observers, is about —113° C., both these cooling agents may be said to lower the temperature sufficiently to produce liquid oxygen, provided a pressure of the gas above the critical pressure, which is 50 atmospheres, is at command. In any case, however, the temperature is near that of the critical point ; and as it is difficult to maintain the pressure below about an inch of mercury, the temperature is apt to be rather above the respective temperatures of —115° C. and —125° C. In order to get liquefaction conveniently with either of these agents, it is necessary to work at a pressure of oxygen gas from 80 to 100 atmospheres, and to have the means of producing a sudden expansion when the compressed gas is cooled to the above-mentioned temperatures. This is brought about by the use of an additional stopcock, represented in the figure at B. During the expansion the stopcock at A is closed and the pressure-manometer carefully observed. No doubt liquid nitrous oxide is the most convenient substance to use as a cooling agent; but as it is apt to get superheated during the reduction of pressure and boil over with explosive bursts of vapour, it is well to collect the fluid in a small flask of about 250 cub. centim. capacity, and to change it into the solid state by connecting the flask with the air-pump, and then to use the substance in this form. The addition of alcohol or ether to the solid nitrous

oxide makes the body more transparent, and thereby favours the observations.

It is evident that this apparatus enables the observer to determine the density of the fluid gases condensed in the tube F; since he has only to measure the volume of fluid in F, and to collect, by means of the stopcock B, the whole volume of gas given by the fluid and condensed vapour, which gives an accurate determination of the total weight of substance distributed between fluid and vapour in the whole apparatus. The amount of substance which is required to produce the vapour is easily found by observing the vapour-pressure of the liquid gas before expanding it into gas for the volume measurement; and while keeping shut the stopcock B, by opening A suddenly until this pressure is just reached and then instantly shutting off the receiver. If this volume of gas is now measured by opening B as before, the difference between the two volumes thus collected will correspond to the real weight of substance in the liquid state. A rough experiment with oxygen near the critical point gave the density 0·65.

As to the most convenient substance for use as a cooling agent, I am still of opinion that marsh-gas would be the best; and I may take the opportunity of pointing out that the employment of this body was suggested by me in a communication made to the Chemical Section of the British Association in 1883. The following extract from ' Nature,' of October 4, 1883, will prove that my experiments with liquid marsh-gas were made a year in advance of those made recently by M. Cailletet [*] and M. Wroblewski[†]:—

" Professor Dewar pointed out an important relation between the critical temperatures and pressures of volatile liquids and their molecular volumes. The ratio of the critical temperature to the critical pressure is proportional to the molecular volume, so that the determination of the critical temperature and pressure of a substance gives us a perfectly independent measure of the molecular volumes. Prof. Dewar pointed out the great advantage of employing a liquid of low critical temperature and pressure such as liquid marsh-gas for producing exceedingly low temperature. He hoped to be able to approach the absolute zero by the evaporation of liquefied marsh-gas whose critical temperature was less than $-100°$ C., and whose critical pressure was only 39 atmospheres."

I ought to mention that the marsh-gas used in my experi-

[*] " Sur l'emploi du Formène pour la production des très basses températures," *Comptes Rendus,* June 30, 1884.

[†] " Sur les propriétés du gaz des marais liquide, et sur son emploi comme réfrigérant," *Comptes Rendus,* July 21, 1884.

ments was made by the action of water on zinc methyl, and was therefore very pure, and that the observed critical pressure was not 39 atmospheres, but 47·6. The following table gives the values of the ratio of the absolute critical temperature to the critical pressure in the case of a number of substances. The values for ammonia, sulphuretted hydrogen, cyanogen, marsh-gas, and hydride of ethyl are new.

	T, Critical temperature.	P, Critical pressure.	$\frac{T}{P}$.
Chlorine.................... Cl_2	141·0	83·9	5·0
Hydrochloric acid ...... HCl	52·3	86·0	3·7
Oxygen .... O_2	−113·0	50·0	3·2
Water .... H_2O	370·0	195·5	3·3
Nitrogen .... N_2	−146·0	35·0	3·6
Hydrogen sulphide ...... H_2S	100·2	92·0	4·0
Ammonia .... H_3N	130·0	115·0	3·5
Diethylamine........$(C_2H_5)_2HN$	220·0	38·7	15·4
Nitrous oxide .... N_2O	35·4	75·0	4·1
Sulphurous acid .... SO_2	155·4	78·9	5·4
Marsh-gas .... CH_4	− 99·5	50·0	3·5
Acetylene .... C_2H_2	37·0	68·0	4·5
Ethylene .... C_2H_4	10·1	51·0	5·5
Ethyl hydride .... C_2H_6	35·0	45·2	6·8
Amylene .... C_5H_{10}	191·6	33·9	13·7
Benzol .... C_6H_6	291·7	60·4	9·3
Chloroform .... $CHCl_3$	268·0	54·9	9·9
Carbon chloride .... CCl_4	282·0	57·6	9·6
Carbonic acid .... CO_2	31·9	77·0	4·0
Bisulphide of carbon ... CS_2	277·7	78·1	7·0
Cyanogen .... C_2N_2	124·0	61·7	6·4

A glance at the last column of the table shows that a large number of substances have at their respective critical temperatures simple volume relations. Thus hydrochloric acid, water, ammonia, and marsh-gas, the four chemical substances from which the great majority of chemical compounds may be derived by processes of substitution, have nearly the same volume ; while the more complex derivatives show an increased volume which bears a simple ratio to that of the typical body. As the critical pressures are not known with any great accuracy at present, it would be useless to discuss the results with any severity. All that can be inferred is that the subject is worthy of further investigation and promises important generalization. Sarrau (*Compt. Rend.* 1882) deduced the critical temperatures and pressures of hydrogen, oxygen, and nitrogen by the application of Clausius' formula to the experiments of Amagat; and it is interesting to compare his results with the experimental values.

Sarrau's Calculated Values.

	T, Critical temperature.	P, Critical pressure.	$\dfrac{T}{P}$.
Hydrogen	$-17\overset{\circ}{4}$	98·9	1·0
Oxygen	$-105\cdot4$	48·7	3·4
Nitrogen	-124	42·1	3·5

It will be observed that the calculated critical temperatures of oxygen and nitrogen are remarkably near the truth, being respectively 8° and 22° too high. On the other hand, the values of the ratios of the calculated critical temperatures and pressures are almost identical with those obtained by direct experiment. The only peculiarity to be noted is in the case of hydrogen, which has such a high critical pressure, and therefore leads to a remarkably small molecular volume at the critical point. If the values of the T÷P ratio be taken as proportional to the molecular volumes, then it is easy to infer the densities of the fluids at their respective critical temperatures, provided the density of one standard substance is known by experiment. The simple formula thus stated is

$$\frac{S'}{S} = \psi \frac{W'}{W}, \quad \psi = \frac{V}{V'},$$

where S and S' are the specific gravities of two bodies, W and W' their molecular weights, and V and V' their molecular volumes. It will be convenient to take the density of carbonic acid at the critical point as the standard density to which the others can be referred. The density of carbonic acid under such conditions may be taken as 0·65. Calculating with the above formula, the density of acetylene would be 0·32, whereas the experimental number of Ansdell is 0·36. In the same way the density of hydrochloric acid is found to be 0·6, the true value being 0·61. The density of oxygen would be 0·63, and that of nitrogen 0·45. The calculated density of hydrogen at its critical point would be 0·12, if we assume the correctness of Sarrau's values for the critical temperature and pressure. We may compare these values with the numbers obtained by Cailletet and Hautefeuille for the densities of oxygen, nitrogen, and hydrogen from their experiments on the density of liquid carbonic acid obtained from mixtures of this body with these gases. At the temperature of 0° C. the experiments found for oxygen, nitrogen, and hydrogen the respective values of 0·65, 0·37, and 0·025. It

seems that the calculated values for oxygen and nitrogen
are not very far wrong; but hydrogen is clearly incorrect.
The explanation of this anomaly is probably to be found in
the fact that the calculated molecular volume of hydrogen is
wrong, and that instead of being unity on our scale it ought
to be 3·5 like oxygen and nitrogen.   In fact, the chemist
would infer that, as the difference in the complexity of the
molecular structure of hydrochloric acid, water, ammonia, and
marsh-gas does not affect the molecular volume under the
conditions we are discussing, in all probability the value for
hydrogen would be identical with that of the above-mentioned
bodies.   If we adopt this view and change the value of the
$T_c \div P_c$ to 3·5, then the density of the fluid would become
0·034, which is in accordance with the experimental number
of Cailletet and Hautefeuille.   An accurate determination of
the critical temperature and pressure of hydrogen, for which,
judging from the success of the experiments of M. Olzewski,
chemists will not have to wait long, will thus be of great
interest.

XXIX. *A Magneto-electric Phenomenon.*   *By* C. V. Boys,
   *A.R.S.M., Demonstrator of Physics at the Science Schools,
   South Kensington*[*].

EVERY one is familiar with the effect produced when a
   copper disk is set to spin in a powerful magnetic field :
the currents induced by the motion of the disk act in such a
direction as to oppose the motion, which therefore speedily
ceases.   Faraday observed that if, instead of being set to spin,
a disk is merely suspended between the poles of an electro-
magnet, it will in general be disturbed whenever the current in
the coils of the electromagnet is made or broken.   If it lie with
its plane parallel or at right angles to the lines of force, no
disturbance will be apparent if the lines of force where they
are included by the disk are parallel.   But if the plane of the
disk makes an angle α with the parallel lines of force, then on
making the current in the electromagnet an impulse is given
tending to diminish the angle α, while breaking the current
gives an impulse tending to increase the angle α.

   Again, if the angle α be 90°, so as to eliminate this twisting
effect, no movement will be visible at the making or the break-
ing in a parallel field ; but if the disk be placed in a field with
diverging lines of force, in which, of course, the strength
diminishes as the lines separate, and if it be placed symme-
trically so as to include the greatest number (*i. e.* with its

   [*] Communicated by the Physical Society.   Read June 28, 1884.

plane at right angles to those lines passing through its centre), then, on making the current, it will receive an impulse causing it to move parallel to itself along the lines of force towards the weaker part of the field, and at the breaking it will receive an impulse more evident in the opposite direction. If this radiating field is produced between a pointed and a flat pole, the disk will, on making the current, appear to be repelled from, and, on breaking, to be attracted by, the pointed pole. So powerful is this effect that a piece of impure copper, which is strongly magnetic, is repelled from the pointed pole on making, and attracted on breaking, the current, thus appearing at first sight strongly diamagnetic.

Though these impulses must have been observed by most experimentalists, their amount has not been, so far as I am aware, determined in absolute units, nor have they been turned to account for making any measurements. As they seem to afford one of the most convenient methods of determining conductivity and field-intensity, perhaps a short paper on the subject, even though it be incomplete, may be of interest to this Society.

The explanation of the motions described will be obvious, but it may be well to give it at length for the sake of arriving at quantitative results. In the first place, let the lines of force be parallel, so that the field is of uniform strength. Let a ring of (small) section s, of specific resistance ρ, and of radius r, be placed in the field, with its plane making an angle α with the lines of force. Let the strength of the field be H units. Then during a small increment of field-intensity dH, in the time dt, a current will be induced in the ring of the strength

$$\frac{rs \sin \alpha}{2\rho} \frac{d\mathrm{H}}{dt}.$$

This current in the field H will produce a twisting tendency to increase α with a diminishing, or to diminish α with an increasing field, represented by the couple

$$- \frac{\pi r^3 s\mathrm{H} \sin 2\alpha}{4\rho} \frac{d\mathrm{H}}{dt}.$$

From this it is clear that the couple varies inversely as the time dt occupied in making any small change of field-intensity dH, but it lasts for the time dt; therefore the momentum acquired by the suspended disk, if free to move, will be independent of the rate at which any small change in the magnetic field may be made, but will depend only on its amount, provided that the time is not sufficient for the angle α to have perceptibly altered during the change. Since this is true of any element, it is true of all; so the momentum acquired by

the ring is a direct measure of any total change in the strength of the field in which it lies, no matter by what law it changes in strength. If at the end of any rapid change the field remains of any strength, the motion of the ring will be rapidly stopped by the well-known damping action, of which I shall have more to say later. If, however, the field sinks to zero, or nearly so, the momentum acquired can be measured and the original intensity determined.

The current induced in the ring will of course react on the field and bend the lines of force in such a manner as to hinder their passing through its edge, that is to delay the change of included field-intensity; but the impulse is independent of the time or the manner in which the field changes, so it cannot be effected to any extent by this cause.

Since the impulse given to the disk during any element of time is

$$-\frac{\pi r^3 s H \sin 2\alpha}{4\rho} \frac{dH}{dt},$$

the total impulse while H changes between 0 and H will be

$$-\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho}.$$

If the moment of inertia of the disk be M, and the torsional value of the supporting wire be T, the angular velocity ω generated will be

$$\omega = -\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho M},$$

and the throw of the ring θ will be

$$\theta = -\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho \sqrt{MT}}.$$

The action on a disk may be considered as the sum of the actions on the several elementary rings of which it is composed, for there cannot be any tendency for any part of the currents to cross over the elementary circles. The impulse therefore on a disk of radius r and thickness s will be

$$-\frac{\pi r^4 s H^2 \sin 2\alpha}{32\rho};$$

and the impulse on a disk of radius r_2 with a concentric hole of radius r_1 will be

$$-\frac{\pi s H^2 \sin 2\alpha}{32\rho}(r_2^4 - r_1^4).$$

Since the moment of inertia of a disk is also proportional to the fourth power and to the thickness, so long as the thickness is small, it will appear that the velocity imparted to a disk of any size or thickness, or to a ring, during a change in a magnetic field will be the same. To what extent a correction should be applied to these results for self-induction between different parts of the disk I am not prepared to say; their calculation would give trouble.

For comparing one field with another, disks or rings of metal may be used; but for absolute measurements, as it would be impossible to measure the exact conductivity of a disk, a coil is preferable. By employing disks of different metals their conductivities can be compared without the trouble of drawing into wire or cutting into long strips.

It will be found that a coil of area A and resistance R will, under a torsion T, experience a throw

$$\theta = -\frac{A^2 H^2 \sin 2\alpha}{4R\sqrt{MT}}.$$

If, instead of a disk, a sphere be used, no twisting should be experienced if the conductivity in different directions is the same. If, however, there is a plane of greatest or least conductivity, it should be possible to discover it. Crystallization or mechanical treatment might give rise to such planes in metals; no definite results could be expected in any thing else.

I have referred to the apparent repulsion and attraction of a disk of metal by a pointed pole at the making and breaking of the magnetizing current. As the lines from such a pole radiate outwards, they are not normal to the metal except in the middle. On their passage inwards or outwards they give rise to circular currents tending to move each part of the disk normally to the lines of force. There is therefore a longitudinal component away from the point of radiation during an increase in the field, and towards it during a diminution of the field. A closed coil of wire is subject to the same forces. If a coil be made of uncovered copper wire in the form of a double helix with the ends joined together, and if the convolutions are separate so as nowhere to touch one another, the growth of the magnetic field can be watched by placing the coil nearly over one pole. On making the current the field begins to grow, at first quickly and afterwards more slowly. The coil will receive a push and will extend itself. As the push diminishes in amount, owing to the diminishing rate of growth of the magnetic field, the coil will gradually regain its former shape. It might be thought that the slow recoil is simply due to the damping action of the field; but this is not sufficient

to account for it, as when the field is fully grown the coil will, on being forcibly drawn out, recover its shape much more quickly. On breaking the magnetizing current, the impulse in the opposite direction, being the same as before but lasting for so much shorter a time, is far more evident.

My first experiments were made with a view to determine whether the impulse was proportional to $\sin 2\alpha$ when other things remained the same. I therefore cemented a disk of metal (a half-crown) to an ebonite rod carrying a glass index and hung by a torsion-wire of platinum. The glass index travelled over a card divided into degrees; and the wire to which the upper end of the torsion-wire was soldered also carried a pointer, the position of which could, if desired, be read on a divided card. The disk was suspended between two parallel polar faces of iron. The upper index was turned until, on making and breaking the current, the lower index showed no sign of motion. It could thus be placed within a small fraction of a degree, so that α was either $90°$ or $0°$. The lower card was then adjusted, and the upper index turned so that the lower rested successively at $5°$, $10°$, $15°$, &c. up to $90°$. The negative impulse on making, and the positive impulse on breaking, the current were observed by the throw of the lower index. These are given in the second and third columns of the following Table. In the fourth column is a series of numbers in the proportion of $\sin 2\alpha$, the largest number being made to agree with the observed positive throw.

TABLE I.

Position of rest.	Negative throw.	Positive throw.	Calculated positive throw.
5	1	4·5	4·6
10	2	9	9·1
15	3	13	13·2
20	4·5	17	17·1
25	5	20	20·3
30	6	22·5	23
35	7	24·5	25
40	7·8	26·2	26·2
45	8·8	26·5	26·5
50	8·5	26·2	26·2
55	8·2	24·5	25
60	7·8	22	23
65	7·5	20	20·3
70	6·5	16	17·1
75	5·5	12·5	13·2
80	3·5	9	9·1
85	2	4	4·6

The close agreement of the other numbers shows clearly

that, on breaking the circuit, the impulse is truly proportional to sin 2α. Examination shows that the negative impulses, though in reality equal to the others, are apparently much less in amount, that they are not even in proportion, and not only this, but that the corresponding values on either side of 45° are not the same. This want of symmetry is clearly shown by fig. 1. The discrepancy is due to the fact that the disk is brought to rest by the damping action of the field as well as by the torsion of the wire, and that the damping action is greater as the angle is less, being : : $\cos^2 \alpha$.

Fig. 1.
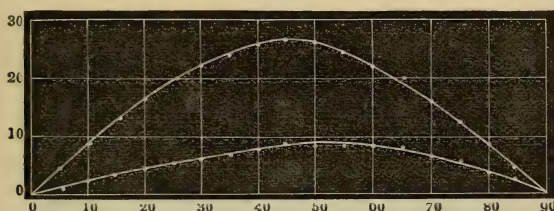
I thought it would be interesting to determine to what angle the disk would be thrown if the torsion of the wire did not act. I therefore suspended, instead of the disk, the coil used in the absolute experiments by a silk thread, adjusted the lower card by the method of no throw, and brought the index to rest successively over 10°, 20°, 30°, &c. up to 90°. The index came to rest at the series of positions shown in column 2 of the following Table:—

TABLE II.

Pointer fell	
From	To
10	3·6
20	6
30	10
40	13
45	16
50	18
60	22
70	29
80	39

The same results are shown graphically in fig. 2. It is

interesting to note that the curve shown is a natural curve depending on circular functions only. It is independent of the nature of material, such as conductivity, moment of inertia, or of the strength to which the field is made to grow from zero. It is subject to a small error, for I did not destroy the residual magnetism. That the effect of this is appreciable is evident, for in one series of experiments with a disk the throw on making was always from 45° to 33°; but the first time that the direction of the magnetizing current was changed the throw was from 45° to 35°, after which it was from 45° to

Fig. 2.
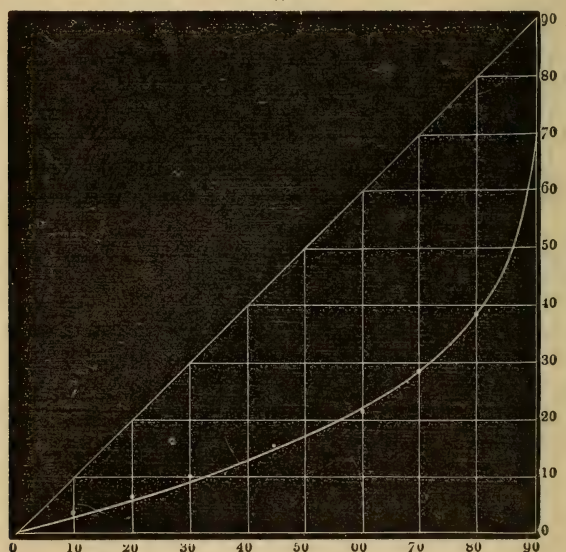
33°, as before. This diminution at the first reversal was always the same. I found almost the same fall with the half-crown as with the coil, and with one cell as with ten cells. There were slight differences, but not more than draughts from which I did not shield the needle would have accounted for. The lower angle can be read with precision, but the higher angles become difficult to observe as the damping influence diminishes. The position $\alpha = 90°$ is one of instability; for however slight a velocity is given to the disk, it will not be brought to rest for a considerable time, owing to the very minute nature of the squares of the cosines of angles nearly equal to 90°.

The last series of experiments was made with a view to determine whether the strength of field determined by observation of the throw of the disk at breaking agreed with the

strength determined by some recognized method. I therefore made a small coil of twelve turns of copper wire of 1·45 centim. radius and with a resistance of 0·085 ohm. The area of the coil was 79·4 square centim. The moment of inertia of coil and index was found by comparison with a cylinder to be 58·1 units, and the torsional value of the supporting wire to be 17,000 units. The plane of the coil was adjusted by the usual method to zero, and then set to 45°. The currents from 10, 9, 8, &c. to 1 Grove cells were sent in succession through the coils of the electromagnet and through a Siemens electrodynamometer. The following Table shows the amounts of the positive and negative impulses, the strengths of the magnetizing currents in amperes, and the field-intensities calculated from the positive throws by the formula

$$H^2 = 9311000 \times \text{Throw measured in degrees.}$$

TABLE III.

Number of cells.	Magnetizing current, in amperes.	Negative throw.	Positive throw.	Calculated field, in absolute units.
10	11·85	10·5	27·5	16,000
9	11·2	9	26	15,600
8	10·44	8·2	24·5	15,100
7	9·47	7	22·5	14,500
6	8·63	6	21·3	14,100
5	7·60	4·8	19·2	13,400
4	6·53	3·3	16·5	12,400
3	5·18	2·2	13	11,000
2	3·67	1	8	8,630
1	1·83	0·2	2·8	5,070

The ends of the coil which were soldered together were then unsoldered without disturbing the soldered connexion between the torsion-wire and one end. The other end was bent so as to dip into a small mercury-cup in the axial line, so that a known current, measured by a second electrodynamometer, could be sent through the coil. During this change no part of the apparatus was moved at all ; it was, however, necessary to redetermine the zero position, which was now rather more difficult, for the resistance of the torsion-wire was so great in comparison with that of the coil alone, that the throw at any angle was only about one tenth of what it was before. As before, the current from 10 to 1 cells was sent successively through the coils of the electromagnet and an electrodynamo-

meter.   The current from a Daniell cell was sent through the
suspended coil and measured.   In the fourth column of the
following Table will be found the deflection of the coil due to
currents tabulated in columns 2 and 3.   In the fifth column
is the deflection due to the residual magnetism; and in the
sixth column the strength of field in absolute units, calculated
from the formula

$$H = \frac{3 \cdot 73 \times \text{deflection in degrees}}{\text{deflecting current in absolute units} \times \cos \delta}.$$

Table IV.

Number of cells.	Magnetizing current, in amperes.	Deflecting current, in amperes.	Deflection $= \delta$.	Deflection due to residual magnetism.	Calculated field, in absolute units.
10	11·92	·514	65	4	11,200
9	11·05	·530*	64	4	10,260
8	10·52	·502	63	4	10,320
7	9·48	·496	62·5	4	10,150
6	8·63	·480	61·5	4	10,050
5	7·60	·480	60·3	4	9,470
4	6·45	·480	59	4	8,930
3	5·14	·480	57	4	8,120
2	3·67	·480	51·5	4	6,470
1	1·98	·480	40·5	4·5	4,140

* Obviously over-estimated, hence small results.

The residual magnetism was always the same till one cell only
had been employed to excite the electromagnet, when the
deflection was clearly greater.   This I repeated several times
with one and with more than one cell : a deflection of $4\frac{1}{2}°$
was always obtained from one cell, and of 4° from more than
one cell.   To obtain a still higher residual magnetic effect, I
drew the terminal along a fine wire and gradually diminished
the field ; by this means I obtained a residual field giving a
deflection of 5°·4.   The magnetic fields corresponding to
the deflections 4, $4\frac{1}{2}$, and 5·4 are 312, 352, and 422 absolute
units.

Fig. 3 shows the field-intensity measured by the two
methods.   They do not agree, nor are they quite proportional,
nevertheless they are of the same order of magnitude.   The
discrepancy is greater than would be expected from errors of
an experimental kind, even though the apparatus was hastily

improvised. Nevertheless the agreement, such as it is, shows that it will be worth while to carry out a series of experiments

Fig. 3.
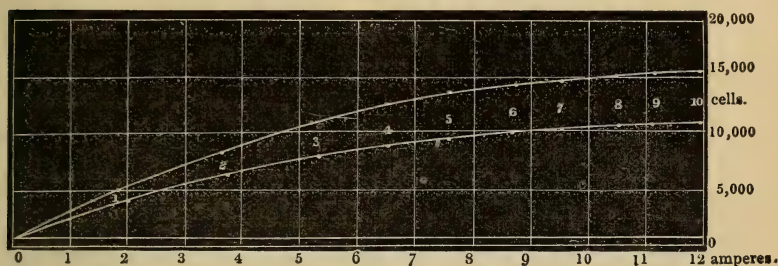
with the accuracy and care that are needed in physical investigations. This I intend to do as soon as I am able. It will then perhaps be possible to tell whether this method of determining conductivity or field-intensity is to be relied upon : it certainly in convenience and simplicity compares very favourably with any of the usual methods.

XXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 159.]

April 2, 1884.—Prof. T. G. Bonney, D.Sc., F.R.S., President, in the Chair.

THE following communications were read :—
1. " The Rocks of Guernsey." By the Rev. E. Hill, M.A., F.G.S. With an Appendix on the Microscopic Structure of some of the Rocks, by Prof. T. G. Bonney, D.Sc., F.R.S., Pres.G.S.

The southern part of the island is a high plateau consisting entirely of gneiss. This is very coarse, and the bedding is seldom well marked. The bedding, when visible, coincides with the foliation, and the author hopes that hereafter an order of succession may be established. At Rocquaine Castle occur a few slaty beds intercalated in the gneiss, the origin of which is somewhat difficult to understand. The northern part, low ground with hummocks, consists principally of a group of crystalline or subcrystalline rocks, in constitution diorites or syenites. They are described by Ansted as sedimentary rocks metamorphosed into syenites ; but they show no bedding either in the many quarries, or, in general, in the shore outcrops, nor do their varieties occur in any manner indicating an order

of succession. They appear at Castle Cornet to meet the gneiss intrusively, and their microscopic structure is igneous. A remarkable appearance of bedded structure at Fort Doyle is the only strong argument for a metamorphic origin, and this may be explained as a caught-up mass in conjunction with crushing-planes. The author therefore regards them as igneous.

An oval area between St. Sampsons and St. Peter's Port is occupied by hornblendic rocks, locally called "birdseye," which may be described as hornblende-gabbros. These also have been called metamorphic. They too, at Hogue-à-la-Perre and at another point, present appearances of bedding; but on the same general grounds as for the preceding group, these also are regarded as igneous.

Two granitic masses are described: the coarse pink granite of Cobo, on the west coast, and the finer-grained grey granite weathering pink of Lancresse, on the north. Each is seen to intrude: the Cobo granite into gneiss at Hommet Barracks; the Lancresse granite into diorite at Fort Le Marchant. Besides these are some smaller masses.

Dykes are remarkably abundant and various. Granites and elvans are plentiful everywhere; felsites very rare. The majority of the dykes are diorites, varying in coarseness and often of enormous size; there is also mica-trap. In some of these dykes a cleavage has been developed, so that some resemble slates. Infiltration-veins are abundant.

In relative age the gneiss appears to be the oldest rock, the hornblende-gabbro to be next, then comes the diorite group, while the granites are newer still. Of the dykes the newest are the compactest diorites. As to the absolute geological age of the rocks no satisfactory evidence at present is known; it will have to be sought for in the other islands and in France.

2. "On a new specimen of *Megalichthys* from the Yorkshire Coalfield." By Prof. L. C. Miall, F.G.S.

3. "Studies on some Japanese Rocks." By Dr. Bundjiro Kotô. Communicated by Frank Rutley, Esq., F.G.S.

The author has studied series of Japanese rocks from the collection of the Tokio University and the Geological Survey of Japan. The microscopical investigation was carried on at the Mineralogical Institute of Leipsic, under the direction of Prof. Zirkel, and the chemical analyses were made in the laboratory of Prof. Knop.

The most abundant rocks are the pyroxene-andesites, which are not of a glassy texture, but for the most part holocrystalline. The most abundant mineral in these rocks is a plagioclase felspar with twinned and zonal structure, which is proved by its extinction-angles and by the chemical analysis of its isolated fragments, to be labradorite. Sanidine is present in small quantities.

The augites of these rocks present many peculiarities; they are all decidedly pleochroic; and they exhibit the oblique extinction in

basal sections, first pointed out by Mr. Whitman Cross, and which is characteristic of triclinic and not of monoclinic crystals. A careful examination of the question has led the author to conclude that the mineral which has lately been regarded as a rhombic pyroxene (probably hypersthene) is really only ordinary augite cut parallel to the optic axis. He does not regard the property of pleochroism as distinctive of hypersthene, while the absence of a brachypinacoidal cleavage and the presence of 10 per cent. of lime in the mineral forbids our referring it to that species.

The other abundant minerals in these augite-andesites are magnetite, which is always present, and quartz, which occurs in some of them, both as a primary and a secondary constituent. Hornblende is very rare in these rocks, and when present the peripheral portions of the crystals are seen to be converted into augite, probably by the action of the caustic magma upon them. Enstatite is rare in these rocks, but apatite is always found in them, while tridymite occurs not unfrequently.

The author described a number of structural variations in the augite-andesite from different localities. Among the most interesting is a variety containing as much as 69 per cent. of silica.

Among the less abundant rocks are the enstatite-andesite, the quartz-augite-andesite, and the hornblende-andesites. The plagioclase-basalts of Japan can only be distinguished from the augite-andesites by the presence in them of olivine. Magma-basalts are rare, most of the varieties being of the dolerite type; but under the name of "basalt-lavas" the author describes varieties with a glassy base.

In an Appendix some account is given of a number of pre-Tertiary rocks, including granite, one variety of which contains the new mineral, reinite, of Fritsch (the tetragonal form of the ferrous-tungstate), quartz-mica-diorite, diorite-porphyry, and diabase.

April 23.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

The following communications were read :—

1. "On the Geology of the Country traversed by the Canada Pacific Railway, from Lake Superior to the Rocky Mountains." By Principal J. W. Dawson, C.M.G., F.R.S., F.G.S.

This paper recorded observations made by the author with reference to the geology of the north-west territories of Canada, in an excursion in the summer of 1883, along the line of the Canada Pacific Railway as far as Calgary, at the eastern base of the Rocky Mountains.

After referring to the labours of the Canadian Geological Survey, and more especially of Dr. G. M. Dawson, F.G.S., in this region, the author proceeded to notice the Laurentian, Huronian, and other Pre-Silurian rocks of the west of Lake Superior and the country between that lake and the Red River. Good exposures of many of

these rocks have been made in the railway-cuttings, and important gold-veins have been opened up. The Laurentian rocks present a remarkable uniformity of structure over all the vast territory extending from Labrador to the Winnipeg river, and where they reappear in the mountains of British Columbia. They are also similar to those of South America and of Europe; and there was on the table a collection of Laurentian rocks from Assouan, in Upper Egypt, made by the author in the past winter, which showed the reappearance of the same mineral characters there. In Egypt there is also an overlying crystalline series, corresponding in some respects with the Huronian. The Huronian rocks west of Lake Superior are, however, more crystalline than those of Lake Huron, and may be of greater age.

The Palæozoic rocks are exposed in places on the western side of the old crystalline rocks near the Red River, and show a remarkable union and intermixture of Lower and Upper Silurian forms, or rather, perhaps, a transition from the one fauna to the other in a very limited thickness of beds. The collections of Mr. Panton, of Winnipeg, were referred to in this connexion.

The Cretaceous and Eocene beds of the plains were then noticed, and certain sections showing the coal-bearing series described; and comparisons were instituted between the Cretaceous and Eocene succession in Canada and that in the United States and elsewhere.

The Pleistocene drift deposits constitute a conspicuous feature on the western prairies. Along the railway, Laurentian, Huronian, and Palæozoic boulders from the east may be seen all the way to the Rocky Mountains, near which they become mixed with stones from these mountains themselves. The vast amount of this drift from the east and north-east, and the great distance to which it has been carried, as well as the elevation above the sea, are very striking. The great belt of drift known as the Missouri Coteau is one of the most remarkable features of the region. It was described in some detail where crossed by the railway, and it was shown that it must represent the margin of an ice-laden sea, and not a land-moraine, and that its study has furnished a key to the explanation of the drift deposits of the plains, and of the so-called "Terminal Moraine," which has been traced by the geologists of the United States, from the Coteau round the basin of the Great Lakes to the Atlantic.

2. "On the Dyas (Permian) and Trias of Central Europe and the true divisional line of these two formations." By the Rev. A. Irving, B.Sc., B.A., F.G.S.

The author, having shown (in previous papers, which appeared in the 'Geological Magazine' during the year 1882) the inapplicability of the "Permian System" of Murchison to the British Postcarboniferous rocks, and having had reasons for doubting the supposed conformity between the Zechstein and the Bunter in Central Europe (on which Murchison and his collaborateurs have laid so

much stress), has, with the aid of Profs. Geinitz and Liebe and Dr. von Hauer, investigated the subject independently, both by examination of sections in the field, and by the study of the evidence preserved in the Museums, especially those of Dresden, Vienna, and Freiberg. The sections described in this paper are from:—(1) *Silesia* (Ostran), in which Dr. A. Dittmarsch is followed ; (2) *Murane* (Saxony); (3) *Northern Thuringia.* Those in the districts (2) and (3) are from the author's own observation last summer. The stratigraphical evidence shows that there is a *very marked break in time* between the Zechstein and the Bunterschiefer of Murchison, which he included in the " Permian System." Almost every kind of discordance that can possibly occur between two successive series of strata is shown to occur in Central Europe between the Dyas and Trias, and in particular between the Bunter and the Zechstein ; physical and stratigraphical evidence therefore confirm the classification adopted by Geinitz on palæontological grounds.

The meaning of the name " Dyas," which has become well established abroad, was illustrated, since it is often overlooked by English geological writers ; and a dyassic order was pointed out as existing to some extent in the English series.

Some general reasons, based on the *physical* characteristics of the Dyas-group, were given for regarding it as much more closely allied to the preceding Carboniferous than to the succeeding Trias.

The last portion of the paper was more speculative, and in it an attempt was made to trace, in the facts we know of the geology of Central Europe, and the inferences drawn from them, the causes of the apparent anomaly between the fauna of the Post-Carboniferous strata of more northern Europe and that of the Alpine Trias.

XXXI. *Intelligence and Miscellaneous Articles.*

ON THE ELLIPTICITY OF PLANETS. BY L. D'AURIA, LATE GEODETICAL ENGINEER OF THE ITALIAN ARMY[*].

ADMITTING that planets were originally in a fluid state, however heterogeneous their respective masses may be considered, their form of equilibrium, when fluid, must have been such that the direction of the resultant of all the forces acting upon any point of the free surface must have been normal to the surface itself. Now the form of equilibrium of any fluid mass when at rest is the sphere ; and when any fluid sphere is made to revolve around any one of its diameters, it becomes more or less flattened on its axis of rotation on account of centrifugal force. This causes the sphere to become an oblate ellipsoid, whose minor diameter coincides with the axis of rotation itself ; and therefore the equation of any meridian line on the surface of any fluid mass revolving around an axis

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* Communicated by the Author.

of inertia can be expressed by

$$a^2 y^2 + b^2 x^2 = a^2 b^2.$$

Differentiating this equation, we have

$$\frac{dy}{dx} = -\frac{x b^2}{y a^2};$$

and observing that the first member represents the cotangent of the latitude ϕ of a point M whose coordinates are x and y (figure), and that $\dfrac{x}{y}$ represents the cotangent of the latitude θ of the same point referred to the centre of the ellipsoid, we have

$$\frac{\sqrt{1 - \sin^2 \phi}}{\sin \phi} = -\frac{b^2}{a^2} \frac{\cos \theta}{\sin \theta},$$

and

$$\sin \varphi = \frac{\sin \theta}{\sqrt{1 - \cos^2 \theta \, e^2 (2 - e^2)}},$$

where

$$e^2 = \frac{a^2 - b^2}{a^2}.$$
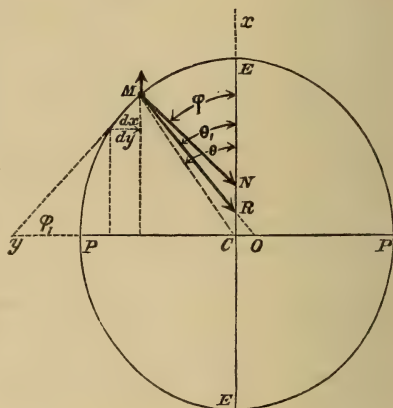
On the other hand, let MR represent the direction and the intensity of the attraction of the whole ellipsoid upon the point M, which attraction we designate by g; and put $MO = \rho$; angle $MRE = \theta_1$; angular velocity $= \omega$. Then the resultant of the attraction g and the centrifugal force at M must coincide with the normal MN, for centrifugal force is parallel to EE; and since this latter force is expressed by $\omega^2 \rho \cos \theta_1$, we have for the resultant itself,

$$f = g \sqrt{1 - \cos^2 \theta_1 \frac{\omega^2 \rho}{g} \left(2 - \frac{\omega^2 \rho}{g} \right)};$$

and therefore

$$\sin \phi : \sin \theta_1 = g : g \sqrt{1 - \cos^2 \theta_1 \frac{\omega^2 \rho}{g} \left(2 - \frac{\omega^2 \rho}{g} \right)};$$

$$\sin \phi = \frac{\sin \theta_1}{\sqrt{1 - \cos^2 \theta_1 \frac{\omega^2 \rho}{g} \left(2 - \frac{\omega^2 \rho}{g} \right)}}.$$

Comparing this value of $\sin \phi$ with the preceding one, we find

$$e^2(2-e^2) = \tan \theta \cotan \theta_1 \, \frac{\omega^2 \rho}{g} \left(2 - \frac{\omega^2 \rho}{g}\right) + \frac{\sin^2 \theta_1 - \sin^2 \theta}{\sin^2 \theta_1 \cos^2 \theta}.$$

When θ and θ_1 become equal to each other, that is when the point M is considered very near to the equator of the ellipsoid, then

$$\frac{\sin^2 \theta_1 - \sin^2 \theta}{\sin^2 \theta_1 \cos^2 \theta} = 0 \, ; \quad \tan \theta \cotan \theta_1 = 1 \, ; \quad \rho = a \, ;$$

and

$$e^2(2-e^2) = \frac{\omega^2 a}{g} \left(2 - \frac{\omega^2 a}{g}\right);$$

$$e^2 = \frac{\omega^2 a}{g}.$$

Since the ellipticity is expressed by $\epsilon = \dfrac{a-b}{a}$, we have

$$2\epsilon - \epsilon^2 = \frac{\omega^2 a}{g}; \; [a]$$

and neglecting ϵ^2, we have, approximately,

$$\epsilon = \frac{\omega^2 a}{2g}.$$

Now, in the case of our planet,

$$\omega = \frac{2\pi}{86184}; \; a = 6,377,278 \text{ metres}; \; g = 9 \text{ metres } 81,462;$$

(including centrifugal force).

Hence
$$\epsilon = \frac{1}{578}.$$

This value is entirely too small compared with $\frac{1}{300}$ as deduced from geodetical measurement of arcs of meridians and parallels. What can be concluded from this? Are we to believe that the theory is false? No, it seems to be in perfect accordance with the conditions of our globe. In fact, if the Earth is at present almost wholly rigid, as Sir W. Thomson has shown it to be, and we admit that, from the time when its mass was wholly liquid, its diurnal rotation has been progressively slowed by the resistance of tides, it follows that, as soon as the liquidity of the mass began to be impaired by the effect of cooling, the flattening could no more

accommodate itself to the diminishing angular velocity on account of the increasing viscosity of the mass. Hence, since that time the theoretical ellipticity of our planet must have been found smaller than the geodetical one; and the discrepancy must have increased to this date, to increase still more with the centuries to come.

Comparing the actual ellipticity with that given by our equation [a], we have a new method for investigating the physical conditions of planets, and the retardation of their diurnal rotations.

Philadelphia, June 7, 1884.

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ON IDUNIUM, A NEW ELEMENT. BY MARTIN WEBSKY.

In a dense bright yellow ore, consisting essentially of zinciferous vanadate of lead, found in the Aquadita mine in the province of Cordova, La Plata, which is found among the minerals brought by Professor Brackebusch from Cordova to Europe, I have detected the presence of a new element allied to vanadium.

If the red metallic acid removed by mercuric nitrate and isolated by heating be treated with caustic ammonia it dissolves, but at first leaves a bright yellow residue, which goes into solution, though more slowly.

The first portion of the solution contains almost exclusively vanadic acid, and, when mixed with a little ammonium sulphide, after a short time black flecks of vanadium oxide.

The subsequent portions give, when mixed with a little ammonium sulphide, after a short time, far more rapidly, purple-red flecks.

The occasion for this experiment was the unusual phenomena observed in the formation of a precipitate resembling silver chloride, and which probably contains this substance; this was met with when, for the purposes of a chlorine determination, the aqueous extract of the soda-smelt of the ore was mixed with silver nitrate and nitric acid, and in still greater quantities on evaporating the second filtrate with hydrochloric acid. After trying a series of suitable and also of some unsuitable processes, the precipitate was found to contain the silver salt of a new metallic acid, which was finally found in the yellow higher oxide, as well as in the lower red one in small quantities.

The new body, to which I assign the name of Idunium, is remarkable for resistance of the silver salt of the higher oxide against reagents, but resembles in its general analytical reactions vanadic acid; in the analytical separation when the latter passes into solution in salammoniac, the idunic acid remains in the mother liquor, and on the addition of ammonium sulphide it becomes red and deposits red idunic oxide.—*Berlin Sitzungsberichte,* June 19, 1884.

XXXII. *On the Chemical Combination of Gases. By* J. J.
Thomson, *M.A., F.R.S., Fellow and Assistant Tutor of
Trinity College, Cambridge*[*].

THE view of chemical combination taken by Clausius and
Williamson, which, as is well known, is that the atoms
which form the molecules of a compound gas are continually
changing partners, possesses many advantages. One of these
is that its consequences can be developed by mathematical
analysis, and that without any further hypotheses many im-
portant results may be deduced. The following paper is an
attempt to develop mathematically some of these conse-
quences; particularly those which concern the effects of
time, pressure, the quantities of the combining bodies present,
and the temperature upon the results of the chemical com-
bination. It can, I think, hardly be doubted that the effects
of these circumstances on chemical combination have been
too much neglected by chemists, and that one of the reasons
why we know so little about chemical affinity is that chemists
have confined themselves to studying the ultimate effects of
any combination, and have neglected the changes which
take place whilst the combination is still going on. To take
a quite analogous case, the science of biology would not be
in its present satisfactory condition if the biologists had
entirely confined their attention to full-grown animals and
had altogether neglected the study of embryology. Of late
years, however, more attention has been paid by chemists to

* Communicated by the Author.

the influence of time, mass, and temperature on chemical combination. Bunsen, Crafts and Meier, Friedel, Guldberg and Waage, Horstmann, Lemoine, Victor Meyer, and others have experimentally investigated one or other of these points. The researches of M. Lemoine on the combination of hydrogen and iodine seem to be the most complete study of a chemical combination which we possess; and I am indebted to M. Lemoine's two papers in the *Annales de Chimie et de Physique*, 5me série, t. xii. and xxvi., for most of the experimental data quoted in this paper. Messrs. Guldberg and Waage, M. Lemoine, M. Horstmann, and Prof. Willard Gibbs have given theories of chemical combination which seem to agree well with the results of experiments.

It is unfortunate that the only case which we can investigate mathematically on direct dynamical principles, viz. the combination of gases, is the one where the difficulties of chemical manipulation are greatest. The following theory is only intended to apply to gases. Before going further it will be well to state what we suppose takes place during chemical combination, for although most of what follows will apply to any theory of the constitution of bodies, yet as it is a great help to be able to form a definite " Vorstellung " of what takes place, we shall assume that the atoms of bodies consist of one or more vortex-rings, and take the view of chemical combination expressed by the following extracts from a book written by the author of this paper ('On the Motion of Vortex-Rings,' pp. 114, 115, 116):—

" When two vortex-rings of equal strength with (as we shall suppose for the sake of simplicity) their planes approximately parallel to each other and approximately perpendicular to the line joining their centres, are moving in the same direction, and the circumstances are such that the hinder ring overtakes the one in front, then if, when it overtakes it, the shortest distance between the circular lines of vortex-core of the rings be small compared with the radius of either ring, the rings will not separate, the shortest distance between their central lines of vortex-core will remain approximately constant, and these circular lines of vortex-core will rotate round another circle midway between them, while this circle moves forward with a velocity of translation which is small compared with the linear velocity of the vortex-rings round it. We may suppose that the union or pairing in this way of two vortex-rings of different kinds is what takes place when two elements, of which these vortex-rings are atoms, combine chemically, while if the vortex-rings are of the same kind, this process is what occurs when the atoms combine to form molecules. If

two vortex-rings paired in the way we have described are subjected to any disturbing influence, such as the action due to other vortex-rings in their neighbourhood, their radii will be changed by different amounts; thus their velocities of translation will become different and they will separate. We are thus led to take the view of chemical combination put forward by Clausius and Williamson, according to which the molecules of a compound gas are supposed not to always consist of the same atoms of the elementary gases, but that these atoms are continually changing partners. In order, however, that the compound gas should be something more than a mechanical mixture of the elementary gases of which it is composed, it is evidently necessary that the mean time during which an atom is paired with another of a different kind, which we shall call the paired time, should be large compared with the time during which it is alone and free from other atoms, which we shall call the free time. If we suppose that the gas is subjected to any disturbance, then this will have the effect of breaking up the molecules of the compound gas sooner than would otherwise be the case. It will thus diminish the ratio of the paired to the free time; and if the disturbance is great enough the value of this ratio will be so much reduced that the substance will no longer exhibit the properties of a chemical compound, but those of its constituent elements. We should thus have the phenomenon of dissociation or decomposition. . . . . It is clear, too, that the value of the ratio of the paired to the free time for the atoms of an elementary gas will have a very great effect on the chemical properties of the gas; thus if the ratio of the free to the paired times for the atoms of the gas be very small the gas will not enter into combination with other gases, for it will only do so to any great extent when the ratio of the free to the paired time for the compound is less than for the atoms in the molecule of the elementary gas; thus we should expect that this ratio would be very small for the atoms of a gas like nitrogen, which does not combine readily with other gases. The value of this ratio would afford a very convenient measure for the affinity of the constituents of a compound for each other. It is also conceivable that this ratio might affect the physical properties of a gas; and in a paper in the 'Philosophical Magazine' for June 1883, I suggested that differences in the value of this ratio might account for the differences in the electric strength of gases.

" Two vortex-rings will not remain long together unless the shortest distance between the central lines of their vortex-

core is small compared with the radius of either of the rings ; now, as the vortex-rings approach each other they alter in size—the one in front expands and the one in the rear contracts. If the rings are to remain together their radii must become nearly equal as they approach each other, and their planes become nearly coincident : it is evident, however, that for this to happen the radii of the rings before they pair must lie within certain limits. The energy of the gas, however, and therefore the temperature, depends upon the mean radius of the vortex-rings which form the atoms of the gas, and, conversely, the mean radius of the vortex-rings is a function of the temperature ; and if the mean radius is between certain limits the temperature must also be between limits ; thus unless the temperature is between certain limits the atoms will not remain long together after they have paired, and so chemical combination will not take place ; this reasoning would indicate that chemical combination could only occur between certain limits of temperature, and this seems to be the case in at any rate a great many cases of chemical combination.

" The following reasoning will explain how it is that the compound after it is formed can exist at temperatures at which the element of which it is composed could not combine. When the elements have once combined, the molecules of the compound will settle down so that the radii of their vortex-atoms will be distributed according to a definite law, and a large proportion of the vortex-atoms will have their radii between comparatively narrow limits, just as, in the ordinary theory of gases, Maxwell's law gives the distribution of velocity. Now suppose that a molecule of a compound of the elements A and B is subjected to any disturbance tending to change the radii of the atoms ; though the difference in the changes in the radii may be sufficient to cause the atoms to separate, yet since the atoms were close together when they were disturbed the difference in the changes must be small; and since the motion is reversible the atom A would only have to suffer a slight change to be able to combine again with a vortex-ring like B, or it could combine at once with a vortex-ring differing only slightly in radius from B. Thus A will have plenty of chances of recombination with the B atoms, and will be in a totally different position with regard to them from that in which it would have been if it had not previously been in combination with a B atom."

As the question of the splitting up of the molecules is a very important one, we shall proceed to consider it more in detail. The configuration of two vortex-rings moving round

each other in the way we have described will tend to alter when the rings are placed in a region where the distribution of velocity is not uniform. Now the configuration may change so that the rings tend to get closer together, or so that they tend to separate: in the first case, as the rings get closer together the effect of the disturbance will be to make the connection between the rings firmer, but in the second case the disturbance will tend to separate the rings. Now let us suppose that we have two rings moving in the disturbed fluid: if the effect of the disturbance be to make the one in front move faster than the one in the rear, then the disturbance will tend to separate the rings; but if the disturbance in the fluid makes the one in front move more slowly than the one in the rear, the effect of the disturbance will be to make the rings cling more closely together. Now the properties of vortex-motion are such that if the distribution of velocity in the fluid is not uniform, then when two vortex-rings are moving together in one direction the effect of the disturbance in the fluid will be to make the ring in front move more slowly than the one in the rear, while when they move in the opposite direction the effects of the disturbance will be to tend to make the ring in front move faster than the one in the rear, and so tend to separate the rings. Thus we see that it follows from our theory of chemical combination that a molecule of a compound gas would tend to split up if it moved in one way, while it would have no such tendency if it moved in the opposite direction. If we take as the disturbance that produced by an electric field, then it follows that those molecules in the field which move in one direction relatively to the lines of electric force will tend to split up or be dissociated, while those moving in the opposite direction will experience no such effect. This, taken in conjunction with the theory of the electric discharge mentioned above, will, I think, account for many of the differences between the positive and the negative discharge ; in this paper, however, I shall confine myself to the more purely chemical effects.

We shall find it important to remember that there are two kinds of dissociation: in the first the molecules are split up by external aid, such as the action of light or electricity ; in the second the body suffers dissociation at a high temperature without there being any external disturbance. It is usual to assume that the increase in the number of collisions is the cause of the dissociation at high temperatures ; but when we come to discuss the experiments on dissociation we shall, I think, see reasons for believing that this is at any rate not

the primary cause. We must remember that even though there were no disturbance two vortex-rings would only stay together for an infinitely long time if the shortest distance between their circular lines of vortex-core were infinitesimally small compared with the radius of the ring; if this were not the case, two rings would separate of themselves after a time, which depends on the ratio of the shortest distance between their circular axes to the radius of the ring. Thus even if the rings suffered no collisions they would come apart after a time; and the experiments seem to show that some such cause as this is, in some cases of dissociation, more effective than the collisions.

§ 1. We shall now go on to consider the subject analytically; we shall take a very simple case to begin with, and treat it in great detail. The case we shall begin with is that of the dissociation of a simple gas whose molecules are diatomic, and we shall suppose that the gas is a mixture of atoms and molecules. The problem of finding the differential equations which would be true for all stages of chemical combination would lead to results of great complexity; we shall content ourselves with investigating the case when things have settled down into some degree of regularity. We shall suppose that the circumstances have become such that during the mean time a molecule is paired the change in the number of molecules is only a small fraction of their whole number. This will not be the case when violent chemical action first commences, but things will soon settle down into a state when this will be true. We shall also suppose that all the atoms remain paired for the same time t and free for the time T: this of course is not, strictly speaking, the case, as the time the various molecules are paired will be different; but if t is proportional to the mean paired time, and T to the mean free time, the general results obtained on this supposition will agree with those obtained on the more accurate hypothesis, which it is impossible to use, as we do not know the expression which tells how many molecules have any particular paired time.

To go back to the case of the dissociated gas, let m be the number of molecules at any time, n the number of atoms at the same time; then if the gas is in a closed vessel, $n+2m$ will be constant and equal to N, the number of atoms there would be if all the molecules were dissociated. Let t and T have the same meaning as before. T will evidently be inversely proportional to n; let it equal τ/n. Now consider what happens in the time δt: in this time $m\delta t/t$ of the molecules will be split up; for, as we suppose the rate of forma-

tion of the molecules to remain approximately constant during the time t, the number of molecules formed in the time x bears to the number formed in the time t the ratio of x to t; but the number formed in t is m, so that the number formed in x is mx/t. But the number of molecules dissociated in the time δt is the same as the number formed in the interval δt, t seconds ago, so that the number of molecules split up in the time δt is $m\delta t/t$. In exactly the same way we see that the number of pairs of atoms which combine in the time $\delta t = n\delta t/T = n^2\delta t/\tau$; so that if δm be the increase in the number of molecules in the time δt, we have

or

$$\left.\begin{aligned} \delta m &= \frac{n^2\delta t}{\tau} - \frac{m}{t}\delta t \\[2mm] \frac{dm}{dt} &= \frac{n^2}{\tau} - \frac{m}{t} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similarly we may prove that

$$\frac{dn}{dt} = \frac{2m}{t} - \frac{2n^2}{\tau}.$$

When things have got into a stationary state $\dfrac{dm}{dt}$ and $\dfrac{dn}{dt}$ both vanish, so that

$$\frac{n^2}{\tau} = \frac{m}{t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since $n + 2m = N$, we have

$$n + \frac{2t}{\tau}n^2 = N. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation will always determine n; if the dissociation is slight, so that the number of atoms is small compared with the number of molecules, we have

$$\frac{2tn^2}{\tau} = N,$$

or

$$\frac{n}{N} = \sqrt{\frac{\tau}{2tN}}.$$

From this equation we see that if τ and t are independent of N, which will be the case if the process is a reversible one, and the dissociation produced by the action of light or electricity, then the ratio of the atoms actually free to the whole number of atoms in the gas is inversely proportional to the square root of the density, the temperature being supposed to

remain constant; or we may say that in such cases the dissociation produced is inversely proportional to the square root of the density.

It will be easy and convenient to express equation (3) as an equation giving the vapour-density of the dissociated gas. Let Δ be the vapour-density of the dissociated gas, D the vapour-density of the gas when it is not dissociated; then

$$\frac{\Delta}{D} = \frac{\frac{N}{2}}{n+m} = \frac{N}{2n+2m} = \frac{N}{N+n};$$

$$\therefore \frac{n}{N} = \frac{D-\Delta}{\Delta},$$

and

$$\therefore \frac{m}{N} = \frac{2\Delta-D}{2\Delta}.$$

Substituting these values for n and m, equation (2) becomes

$$(D-\Delta)^2 = \frac{\tau}{tN}\left(\frac{2\Delta-D}{2}\right)\Delta.$$

Now if p be the pressure of the gas, $p = cN$, where c is a constant; substituting for n we have

$$(D-\Delta)^2 = \frac{\tau}{tcp}\left(\frac{2\Delta-D}{2}\right)\Delta. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Equations (3) and (4) could be applied most easily to the case when the dissociation is produced by external agency, such as light or electricity, because in this case t and τ would be independent of N, and these equations would then give the vapour-density of the gas at different pressures, the disturbance producing the dissociation remaining the same. No quantitative measurements seem, however, to have been made for such a case. Some experiments have been made on the dissociation of iodine-vapour by heat. If the dissociation were due in this case to the collision of the particles, then the paired time would vary inversely as the number of collisions, and therefore inversely as N, so that Nt would be constant, and, as equations (3) and (4) show, the dissociation would be the same at all pressures; the experimental results show that this is not the case, so that from our point of view we cannot assume that the collisions are the cause of the dissociation. Another circumstance which points to the same conclusion is the fact that dissociation is very much hindered by the presence of a neutral gas; if the dissociation were due to shocks,

then the presence of the neutral gas would increase the number of atoms, and therefore the number of shocks, and so would diminish the paired time, while, as we can hardly conceive that the presence of a neutral gas can make the atoms combine more quickly, the free time will not be diminished. Thus if the collision theory were correct, the dissociation would be increased by the presence of a neutral gas. The fact that this is not the case shows that the mere increase in the number of collisions, if the increase be produced by the collision of different bodies, will not produce increased dissociation. We must remember that, as was remarked before, two atoms will not remain together indefinitely, even if there are no collisions. In the following table I have calculated by means of equation (4) the quantity of iodine-vapour which would be dissociated if the paired time were independent of N, and if the collisions were not the cause of the dissociation, and compared them with the experimental results obtained by Crafts and Meier (*Comptes Rendus*, 3 Janvier, 1881, p. 41, quoted by M. Lemoine, *Annales de Chimie et de Physique*, 5me série, t. xxvi. p. 347); the theoretical and the experimental results agree so closely that the difference between them might be accounted for by errors of experiment. The constant $\dfrac{\tau}{ct}$ which occurs in equation (4) is determined by making the theoretical and the experimental results agree at the pressure ·4 of an atmosphere. I have taken D, the vapour-density of normal (*i. e.* not dissociated) iodine-vapour, to be 8·78.

Vapour Density of Iodine at 1250° C.

Pressure in atmospheres.	Density.	
	Observed.	Calculated.
1	5·8	6·12
·4	5·54	5·54
·3	5·30	5·36
·2	5·07	5·15
·1	4·72	4·84

From equation (4) we find, by substituting the observed value of Δ at the pressure of ·4 of an atmosphere, that

$$\frac{\tau}{tN} = \frac{·66}{p},$$

where p is the pressure expressed in atmospheres. So that at the pressure of one atmosphere

$$\frac{\tau}{tN} = \cdot 66.$$

Now

$$\frac{n}{N} = \frac{8\cdot 78 - 5\cdot 8}{5\cdot 8} = \cdot 5 \text{ approximately};$$

$$\therefore \frac{\tau}{n} \Big/ t = 1\cdot 32,$$

or the free time is $1\cdot 32$ times the paired time.

At the temperature of $900°$ C., since $\Delta = 7\cdot 8$ at the pressure of one atmosphere, we find that

$$\frac{\tau}{tN} = \frac{\cdot 014}{p};$$

so that at the pressure of one atmosphere $\tau/tN = \cdot 014$. In the same way as before we find $n/N = \cdot 125$;

$$\therefore \frac{\tau}{n} \Big/ t = \cdot 112,$$

or the free time is only about 1/9 of the paired time.

The close agreement between the observed results and those calculated by equation (4) seems to show that the dissociation in this case is produced by external agency and not by the collision of the molecules themselves. The radiant heat from the sides of the vessel containing the iodine-vapour would tend to dissociate the vapour, and this may be the external agency required. This consideration suggests the view that the absorption of radiant heat by gases may be due, at least in part, to the dissociation of the gas by the radiant heat. This dissociation would absorb energy, and therefore the radiant heat. This view would account for gases whose molecular structures are complex absorbing heat much more powerfully than the elementary gases; for it is very probable that the radiant heat employed in experiments on the absorption of heat by gases is powerful enough to dissociate bodies of complicated structure, but not powerful enough to dissociate the elementary gases. We must, however, leave this subject for the present and return to that of chemical combination.

We have seen how the ratio of the free to the paired time can be determined by observations made when things have settled down into a state of equilibrium. We cannot, however, by observations of this kind determine t and τ separately. To do this we must, as we can see by referring to the diffe-

rential equations (1) and (2), make observations before things have got into a steady state. If the atoms could in any way be withdrawn from the field of action as soon as they are formed—if, for example, they combined with some solid body which had no effect upon the molecules—then we could determine t, the paired time, by measuring the rate at which molecules of the gas must flow into a vessel containing the solid body and the gas undergoing dissociation, in order that the pressure in the vessel should remain constant. For if m be the number of molecules in the vessel, since the atoms are absorbed as soon as produced, the rate at which the molecules diminish is m/t, so that if the pressure is to remain constant molecules must flow into the vessel at the rate m/t; in this way we could determine t. If the chemical action is slow, we might find this quantity in another way. We have by equation (1)

$$\frac{dn}{dt} = \frac{N-n}{t} - \frac{2n^2}{\tau};$$

$$\therefore \frac{dn}{n^2 + \frac{\tau}{2t}n} - \frac{\tau}{2t}N = -\frac{2dt}{\tau}.$$

Integrating this equation we have, if $K = \{\tau N/2t + \tau^2/16t^2\}^{\frac{1}{2}}$,

$$\frac{1}{2K} \log \frac{\left(K + n + \frac{\tau}{4t}\right)}{K - \left(n + \frac{\tau}{4t}\right)} = \frac{2t}{\tau} + c;$$

or if t' be the time required to increase the number of free atoms from n_1 to n_2 we have

$$\frac{1}{2K} \log \frac{\left(K + n_2 + \frac{\tau}{4t}\right)\left(K - \left(n_1 + \frac{\tau}{4t}\right)\right)}{\left(K + n_1 + \frac{\tau}{4t}\right)\left(K - \left(n_2 + \frac{\tau}{4t}\right)\right)} = \frac{2t'}{\tau}.$$

Now K only involves the ratio of τ to t, which we can find by experiments on the steady state. Thus K is known, and this equation will enable us to find τ; and since we know the ratio of τ to t, we shall be able to find t.

§ 2. We can investigate in a similar way the case when the molecules of two compound or elementary gases enter into chemical combination without being previously decomposed, such, for example, as the case when PCl_3 and Cl_2 com-

bine to form PCl_5, or the reverse action when PCl_5 is decomposed into these two gases.

Let us suppose that the molecules of a gas A can combine with the molecules of another gas, B, without either of them being decomposed, and that one molecule of A combines with one of B, to form one of a compound C. Let m, n, p be the number of molecules at any time of A, B, C respectively, let us suppose the gases placed in a closed vessel, and let M and N be the total number of molecules of A and B respectively in the vessel; then

$$m + p = M, \text{ and } n + p = N.$$

Let us suppose that the molecules of A and B remain together in the compound C for a time t, and let a molecule of A remain apart from a molecule of B for the time τ/n; then, just as in paragraph (1), we have

$$\left.\begin{aligned}
\frac{dp}{dt} &= \frac{mn}{\tau} - \frac{p}{t} \\
\frac{dm}{dt} &= \frac{p}{t} - \frac{mn}{\tau} \\
\frac{dn}{dt} &= \frac{p}{t} - \frac{mn}{\tau}
\end{aligned}\right\} \quad \dots \dots \quad (5)$$

Now when things have got into a state of equilibrium

$$\frac{dp}{dt}, \quad \frac{dm}{dt}, \quad \frac{dn}{dt}$$

all vanish, and we have

$$\frac{mn}{\tau} = \frac{p}{t},$$

or

$$(M-p)(N-p) = \frac{\tau}{t}p. \quad \dots \quad \dots \quad (6)$$

This equation gives the quantity of the compound C formed when the elements A and B are mixed in any proportion. To consider the simplest case, first let $M = N$, so that equal quantities of the gases A and B are mixed together, or, what amounts to the same thing, we may suppose that we have initially a quantity of the compound C in a vessel, and then by some means or another it gets dissociated. In this case, putting $M = N$, we have

$$(M - p)^2 = \frac{\tau}{t} p.$$

This case is exactly the same as the dissociation of an elementary gas which we considered in § 1. M. Friedel (*Bulletin de la Société Chimique,* 1875, p. 160, 1876, p. 241, quoted by M. Lemoine, *Annales de Chimie et de Physique,* 5me série, t. xxvi. p. 324) has made a series of investigations on the combination of oxide of methyl with hydrochloric acid; this combination is a case of the kind we are considering, as in this combination one molecule of oxide of methyl combines with one molecule of hydrochloric acid. Let us first compare the results obtained by M. Friedel at different pressures with the results given by equation (6), which may be written

$$(M - p)^2 = \frac{C}{\Pi} p,$$

where Π is the pressure expressed in atmospheres; we suppose, as before, that the collisions do not affect the dissociation. The constant C is determined by making the calculated and observed values of p agree at the pressure of one atmosphere.

Dissociation of the Compound of Oxide of Methyl and Hydrochloric Acid at different temperatures.

Pressure expressed in atmospheres.	Value of m / M.	
	Calculated.	Observed.
·882	·898	·876
1	·860	·860
1·118	·847	·843
1·447	·790	·815

Though the observed and calculated results agree tolerably closely, yet the differences between them, considering the comparatively small range of pressure, seem greater than can be accounted for by errors of experiment, and seem to suggest that in this case the collisions may slightly affect the dissociation.

From these experiments we have

$$\frac{\tau}{tM} = 5 \cdot 28$$

at the pressure of one atmosphere; but at this pressure $m / M = ·86$, so that

$$\frac{\tau}{tm} = 6 \cdot 14;$$

so that for the compound of oxide of methyl and hydrochloric acid at the pressure of one atmosphere the free time is about 6·14 times the paired time.

We will now go on to consider the effects of either the methyl oxide or the hydrochloric acid being in excess. To do this we must use equation (6), viz.

$$(M-p)\ (N-p) = \frac{\tau}{t}\ p.$$

We can calculate the quantity τ/t if we know the quantity of the compound formed when equal quantities of oxide of methyl and hydrochloric acid are present, *i. e.* when $M = N$. We can then, by the use of this equation, determine the quantity which ought to be formed when the methyl oxide and the hydrochloric acid are mixed in any other proportion. In the experiments we shall compare with the results obtained by this equation the methyl oxide was in excess. We shall measure this excess, which we shall call e, by the rate of the difference between the number of free methyl oxide and hydrochloric molecules to the number of hydrochloric molecules in the vessel, so that

$$n = m + e M.$$

Equation (6) then becomes

$$n\ (m + e\ M) = \frac{\tau}{t}\ \{M - m\}\ ;$$

or, if $m/M = x$,

$$x^2 + ex = c(1-x),$$

where $c = \tau t/M$. We determine c by making the formula true when $e = 0$.

Dissociation of the Compound of Methyl Oxide and Hydrochloric Acid.

e.					x.	
					Calculated.	Observed.
0	.	.	.	.	·884	·884
·222	.	.	.	.	·846	·838
·5	.	.	.	.	·822	·833
1·333	.	.	.	.	·784	·761
3·0	.	.	.	.	·764	·661

The agreement of these, with the exception of the last, is as close as could be expected; the last discrepancy, however, seems to show that some circumstances which we have neglected have to be considered, and the most likely one seems to be the effect of the collisions. If this were so, we

might see some reason for a remarkable result obtained by M. Friedel, viz. that the effects when the methyl oxide was in excess were slightly different from those when the hydrochloric acid was in excess. For it is probable that the effects of a collision, when a molecule of a compound is struck by a molecule of methyl oxide, will not be the same as if it be struck by a molecule of hydrochloric acid; so that the effect of the collisions produced when the methyl oxide is in excess will be different from those produced when the hydrochloric acid is in excess.

If there are any solid or liquid substances which unite directly with oxide of methyl or hydrochloric acid, we can determine the values of τ and t by the first method in § 1. We can also determine these quantities if we can find any solid or liquid that will combine with the compound formed by the combination of these gases, and yet not with the gases themselves. For suppose we have a quantity of this solid in a vessel filled with a mixture of equal parts of oxide of methyl and hydrochloric acid, and that the pressure in this chamber is kept constant by allowing oxide of methyl and hydrochloric acid to stream in at a measured rate. Then, since $N = M$, the rate of formation of the compound is N^2/τ; and as it is absorbed by the solid as soon as made, the rate at which either the methyl oxide or the hydrochloric acid must stream in, in order to keep the pressure constant, is N^2/τ; if we measure this quantity, since we know N we can find τ. If we can use neither of these ways we must try the second method of § 1.

The dissociation of the pentachloride of phosphorus PCl_5 into PCl_3 and Cl_2 is another example of the case we are considering; and in the following table the vapour-densities at different pressures calculated by equation (5) are compared with the vapour-densities at those pressures observed by M. Wurtz (*Comptes Rendus*, lxxvi. p. 601). The vapour-density of the normal pentachloride is taken as 7·2, and the observed and calculated results are made to agree at the pressure of 243 millimetres of mercury.

Dissociation of Phosphorus Pentachloride at 137° C.

Pressure in millimetres of Mercury.	Vapour-density.	
	Calculated.	Observed.
281	6·51	6·48
269	6·49	6·54
243	6·46	6·46
234	6·455	6·42
148	6·28	6·47

We find, in the same way as before, that for PCl_5 at 137° C. and under a pressure of 243 millim. of mercury the free time is about ·26 times the paired time.

§ 3. In the cases we have hitherto considered only three systems of particles were present, viz. the molecules of A, B, and C. The next case we shall consider is one which is well illustrated by the combination of hydrogen and chlorine; in this case we have five systems of particles—the atoms and molecules of hydrogen, the atoms and molecules of chlorine, and the molecules of hydrochloric acid. We proceed to investigate this case, using the same principles as in the former.

Let m = the number of hydrogen atoms.

n = the number of hydrogen molecules.

p = the number of chlorine atoms.

q = the number of chlorine molecules.

r = the number of hydrochloric-acid molecules.

t_1 = the time two hydrogen atoms remain paired together in the hydrogen molecule.

t_2 = the time two chlorine atoms remain paired together in the chlorine molecule.

t_3 = the time a hydrogen atom is paired with one of chlorine in the hydrochloric-acid molecule.

$\dfrac{\tau_1}{m}$ = the time during which a hydrogen atom is free from another hydrogen atom.

$\dfrac{\tau_2}{p}$ = the time a hydrogen atom is free from a chlorine atom.

$\dfrac{\tau_3}{p}$ = the time a chlorine atom is free from another chlorine atom.

M = the total number of hydrogen atoms, whether free or in combination with other atoms.

N = the total number of chlorine atoms, whether free or in combination with other atoms.

Then, as in § 2, we have the following equations:—

$$m + 2n + r = M$$
$$p + 2q + r = N$$

$$\begin{aligned}
\frac{dm}{dt} &= \frac{2n}{t_1} + \frac{r}{t_3} - \frac{2m^2}{\tau_1} - \frac{mp}{\tau_2} \\
\frac{dn}{dt} &= \frac{m^2}{\tau_1} - \frac{n}{t_1} \\
\frac{dp}{dt} &= \frac{2q}{t_2} + \frac{r}{t_3} - \frac{2p^2}{\tau_3} - \frac{mp}{\tau_2} \\
\frac{dq}{dt} &= \frac{p^2}{\tau_3} - \frac{q}{t_2} \\
\frac{dr}{dt} &= \frac{mp}{\tau_2} - \frac{r}{t_3}
\end{aligned} \right\} \quad . \quad . \quad . \quad .(7)$$

Let us first consider the case when things have got into a steady state; in this case $\frac{dm}{dt}$, $\frac{dn}{dt}$, $\frac{dp}{dt}$, $\frac{dq}{dt}$, $\frac{dr}{dt}$ are all zero, and the above equations may be written:—

$$\left. \begin{aligned}
\frac{m^2}{\tau_1} &= \frac{n}{t_1} \\
\frac{p^2}{\tau_3} &= \frac{q}{t_2} \\
\frac{mp}{\tau_2} &= \frac{r}{t_3}
\end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

These, with the equations

$$m + 2n + r = M,$$
$$p + 2q + r = N,$$

will be sufficient to determine the five quantities m, n, p, q, r. We shall get much simpler equations if we suppose, as is nearly always the case, that the number of free atoms of hydrogen or chlorine is very small compared with the number of hydrogen or chlorine molecules respectively. Making this assumption, we may write

$$n = \tfrac{1}{2}(M - r),$$
$$q = \tfrac{1}{2}(N - r).$$

Multiplying the first two equations of (8) we get

$$\frac{m^2 p^2}{\tau_1 \tau_3} = \frac{nq}{t_1 t_2}.$$

Using the third equation of (8) we get

$$\frac{\tau_2^2}{\tau_1 \tau_3} r^2 = \frac{t_3^2}{t_1 t_2} nq;$$

or substituting for n and q their values from (8) we have

$$r^2 = \frac{1}{4} \frac{t_3{}^2 \tau_1 \tau_3}{t_1 t_2 \tau_2{}^2} (M - r)(N - r) \quad . \quad . \quad . \quad . \quad (9)$$

Let us first suppose that equal quantities of the two gases hydrogen and chlorine are present, so that $M = N$; in this case equation (9) becomes

$$r = \left\{ \frac{1}{4} \frac{t_3{}^2 \tau_1 \tau_3}{t_1 t_2 \tau_2{}^2} \right\}^{\frac{1}{2}} (N - r) \quad . \quad . \quad . \quad . \quad (10)$$

Now if the decomposition is due to the action of some external disturbance such as light, radiant heat, or electricity, the t's and τ's will not be functions of the pressure, and we shall get an equation for r/N, which does not involve the pressure; thus the proportion of the compound dissociated is independent of the pressure. This case offers, in this respect, a remarkable contrast to the preceding one. But even if the compound were dissociated by heat, and we were to suppose the dissociation produced by the collisions, though we gave reasons before for supposing this view to be erroneous, still since only t_1, t_2, t_3 are affected by the number of collisions, and as they enter into equation (10) in the form $t_3{}^2/t_1 t_2$, we see that unless the ratio of these quantities is altered by the collisions, the dissociation will be the same at all pressures. Thus we should expect that in this case the dissociation will be very much less influenced by pressure than in the preceding one. This has been confirmed by the researches of M. Lemoine on the vapour of hydriodic acid; he found that the dissociation of this compound was only very slightly affected by the pressure.

Equation (9) enables us to find the quantity of hydrochloric acid produced when hydrogen and chlorine are mixed in any proportion, though no quantitive experiments seem to have been made on hydrochloric acid, yet M. Lemoine (*Annales de Chimie et de Physique*, 5$^{\text{me}}$ série, t. xii.) has made a very elaborate series of experiments on the analogous case of the combination of hydrogen and iodine, and we can compare the results of our theory with his experiments. The experimental results given below were made at a temperature of 440° C. We determine the value of $t_3{}^2 \tau_1 \tau_3 / t_1 t_2 \tau_2{}^2$ by making the result given by equation (9), when $N = M$, agree with the experimental results: if we do this we arrive at the following results:—

Combination of Hydrogen and Iodine at 440° C.

Proportion of H and I.	Ratio of free hydrogen to the total quantity of hydrogen.	
	Observed.	Calculated.
H + I	·240	·240
H + ·784I	·350	·342
H + ·527I	·547	·519
H + ·258I	·774	·750

Here the agreement between theory and experiment is as close as could be expected.

We also find from the experimental results that

$$\frac{t_3^2 \tau_1 \tau_3}{t_1 t_2 \tau_2^2} = 40 \cdot 1.$$

We have just seen that $t_3^2 \tau_1 \tau_3 / t_1 t_2 \tau_2^2$ can be determined by observations made when things have settled into a state of equilibrium; we shall require, however, other observations to determine the t's and the τ's separately. Let us suppose that the dissociation is produced by some external agency; then t_1 will be the same for hydrogen alone as for hydrogen and chlorine mixed, and we may suppose that t_1 and t_2 have been determined by experiments on hydrogen and chlorine separately by one of the methods of § 1. Suppose that we have an arrangement for taking the hydrochloric acid away as soon as it is formed (this may be done by absorbing it by water, as in Bunsen's and Roscoe's experiments on the combination of hydrogen and chlorine exposed to the action of light), and that equal quantities of hydrogen and chlorine stream into the vessel where combination occurs at such a rate as to keep the pressure there constant; then if v be the number of molecules of either hydrogen or chlorine which flow into the combination-chamber in the unit of time, instead of equation (7) we have the following set of equations, the notation being the same as before:—

$$v = \frac{m^2}{\tau_1} - \frac{n}{t_1},$$

$$v = \frac{p^2}{\tau_3} - \frac{q}{t_2},$$

$$2v = \frac{mp}{\tau_2};$$

so that

$$\left(v + \frac{n}{t_1}\right)\left(v + \frac{q}{t_2}\right) = \frac{4v^2 \tau_2^2}{\tau_1 \tau_3} . \quad . \quad . \quad (11)$$

S 2

Now if M be the number of hydrogen or chlorine atoms in the vessel where the combination takes place, since m and p are small compared with n and q respectively, we may put $n = q = \frac{1}{2}M$, and equation (11) becomes

$$\left(v + \frac{M}{2t_1}\right)\left(v + \frac{M}{2t_2}\right) = \frac{4v^2\tau_2^2}{\tau_1\tau_3}. \quad . \quad . \quad . \quad (12)$$

Now of the quantities involved in this equation, we know v, M, t_1, t_2, so that it will enable us to find $\tau_2^2/\tau_1\tau_3$; but equation (9) will give us $t_1t_2\tau_2^2/t_3^2\tau_1\tau_3$; hence we can find t_3. We require two more equations to enable us to determine all the t's and τ's. Let α and β be the specific gravities of normal hydrogen and chlorine respectively; then the specific gravities of the hydrogen and chlorine in the vessel where combination takes place, are respectively

$$\frac{\alpha}{1 + \frac{m}{M}}, \qquad \frac{\beta}{1 + \frac{p}{N}};$$

but

$$m^2 = \tau_1\left\{v + \frac{n}{t_1}\right\} = \tau_1\left\{v + \frac{M}{2t_1}\right\},$$

$$p^2 = \tau_3\left\{v + \frac{q}{t_2}\right\} = \tau_3\left\{v + \frac{M}{2t_2}\right\},$$

since, as before, $n = q = \frac{1}{2}M$; thus the specific gravity of the hydrogen in the vessel

$$= \frac{\alpha}{1 + \frac{1}{M}\left[\tau_1\left(v + \frac{M}{2t_1}\right)\right]^{\frac{1}{2}}},$$

that of the chlorine

$$= \frac{\beta}{1 + \frac{1}{M}\left[\tau_3\left(v + \frac{M}{2t_2}\right)\right]^{\frac{1}{2}}},$$

and the specific gravity of the mixture

$$= \frac{1}{2}\left\{\frac{\alpha}{1 + \frac{1}{M}\left[\tau_1\left(v + \frac{M}{2t_1}\right)\right]^{\frac{1}{2}}} + \frac{\beta}{1 + \frac{1}{M}\left[\tau_3\left(v + \frac{M}{2t_2}\right)\right]^{\frac{1}{2}}}\right\}.$$

By observing the specific gravity of the mixture when the pressure is made to vary, *i. e.* when M is made to vary, we shall get equations sufficient to determine τ_1 and τ_3, and then by equation (12) we can find τ_2, so that in this way all the t's and τ's could be determined.

§ 4. Hitherto we have only considered the combination of two monad elements; the same theory will, however, apply to the combination of any two elements of the same quantivalence. We shall now go on to consider the more complex case of the combination of a dyad element with a monad, when two atoms of one are combined with one of the other; as a typical case we may take water, H_2O. Here the question arises, does the combination consist in an atom of oxygen uniting with a molecule of hydrogen, or is it necessary that the hydrogen molecule should be itself split up, and that combination takes place when two atoms of hydrogen meet with an atom of oxygen? We shall suppose that both methods of combination take place, and then, after the investigation is complete, we may deduce either case by giving special values to the constants.

Let m = the number of hydrogen atoms.

n = the number of hydrogen molecules.

p = the number of oxygen atoms.

q = the number of oxygen molecules.

r = the number of water molecules.

M = the total number of hydrogen atoms free and combined.

N = the total number of oxygen atoms free and combined.

t_1 = the time the atoms remain together in the hydrogen molecule.

t_2 = the time two oxygen atoms remain together in the oxygen molecule.

t_3 = the time the atoms remain together in the water molecule before splitting up into a molecule of H and an atom of O.

t'_3 = the time the atoms remain together in the water molecule before splitting up into two free atoms of H and an atom of O.

$\dfrac{\tau_1}{m}$ = the time during which a hydrogen atom is free from another hydrogen atom.

$\dfrac{\tau_2}{p}$ = the time a hydrogen molecule is free from an oxygen atom.

$\dfrac{\tau_3}{mp}$ = the time which elapses before a free hydrogen atom meets simultaneously with another free hydrogen atom and an oxygen atom. This time will be inversely proportional to mp, since if m and p be large, mp is the number of groups,

consisting of one atom of oxygen and one of hydrogen, which can be formed.

$\dfrac{\tau_4}{p}$ = the time during which an oxygen atom is free from another oxygen atom.

Then by the same principles as in § 1 the equations are

$$m + 2n + 2r = M,$$
$$p + 2q + r = N.$$

$$
\left.
\begin{aligned}
\frac{dm}{dt} &= \frac{2n}{t_1} + \frac{2r}{t_3'} - \frac{2m^2}{\tau_1} - \frac{2m^2 p}{\tau_3} \\[4pt]
\frac{dn}{dt} &= \frac{m^2}{\tau_1} + \frac{r}{t_3} - \frac{n}{t_1} - \frac{np}{\tau_2} \\[4pt]
\frac{dp}{dt} &= \frac{2q}{t_2} + \frac{r}{t_3} + \frac{r}{t_3'} - \frac{2p^2}{\tau_4} - \frac{np}{\tau_2} - \frac{m^2 p}{\tau_3} \\[4pt]
\frac{dq}{dt} &= \frac{p^2}{\tau_4} - \frac{q}{t_2} \\[4pt]
\frac{dr}{dt} &= \frac{np}{\tau_2} + \frac{m^2 p}{\tau_3} - \frac{r}{t_3} - \frac{r}{t_3'}
\end{aligned}
\right\} \quad . \ . \ (13)
$$

Let us begin by finding the values of m, n, p, q, r when things have attained a steady state; we shall first assume that the molecule of water is formed by a molecule of hydrogen uniting with an atom of oxygen, and that when a molecule of water is decomposed it splits up into a molecule of hydrogen and an atom of oxygen. These assumptions are represented by making t_3' and τ_3 both infinite, and when things are in equilibrium the above equations become

$$
\left.
\begin{aligned}
\frac{n}{t_1} &= \frac{m^2}{\tau_1} \\[4pt]
\frac{r}{t_3} &= \frac{np}{\tau_2} \\[4pt]
\frac{q}{t_2} &= \frac{p^2}{\tau_4}
\end{aligned}
\right\} ; \quad . \ . \ . \ . \ . \ . \ (14)
$$

so that

$$\frac{r^2}{t_3^2} = \frac{n^2 p^2}{\tau_2^2} = \frac{\tau_4}{t_2 \tau_2^2} n^2 q.$$

Now if we suppose, as in § 3, that the number of free oxygen and hydrogen atoms is very small compared with the

number of oxygen and hydrogen molecules respectively, we may put

$$n = \tfrac{1}{2}(M - 2r),$$
$$q = \tfrac{1}{2}(N - r).$$

So that the last equation becomes

$$r^2 = \tfrac{1}{8} \frac{t_3^2 \tau_4}{t_2 \tau_2^2} (M - 2r)^2 (N - r). \quad . \quad . \quad . \quad (15)$$

It is evident from this equation that the quantity of the compound formed will depend upon the density, for if we make $M = 2N$ we see that the equation can be expressed as an equation in r/M alone; but the coefficients will involve M, so that the value of r/M will depend upon the density. If we suppose that r/M is small we see from equation (15) that r/M increases as M increases, so that a larger proportion would combine at great pressures than at small; or if we look upon it as a case of dissociation we may express the same thing by saying that the dissociation increases as the pressure diminishes. Thus the dissociation of water differs in this respect from the dissociation of hydrochloric acid.

Let us now take the other alternative, and suppose that a water molecule is formed by the union of two separate hydrogen atoms with an oxygen atom, and that when a water molecule is decomposed it splits up into two free hydrogen atoms and an oxygen atom; in this case t_3 and τ_2 are both infinite, and when things have attained a steady state the equations (13) become

$$\left. \begin{aligned} \frac{n}{t_1} &= \frac{m^2}{\tau_1} \\[4pt] \frac{q}{t_2} &= \frac{p^2}{\tau_4} \\[4pt] \frac{r}{t_3'} &= \frac{m^2 p}{\tau_3} \end{aligned} \right\}, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

so that

$$r^2 = \frac{t_3'^2 \tau_1^2 \tau_4}{\tau_3^2 t_1^2 t_2} n^2 p; \quad . \quad . \quad . \quad . \quad (17)$$

or putting, as before,

$$n = \tfrac{1}{2}(M - 2r),$$
$$p = \tfrac{1}{2}(N - r),$$

we get

$$r^2 = \tfrac{1}{4} \frac{t_3'^2 \tau_1^2 \tau_4}{\tau_3^2 t_1^2 t_2} (M - 2r)^2 (N - r), \quad . \quad . \quad (18)$$

which is an equation of exactly the same form as the one we obtained on the first hypothesis; hence we could not distinguish between these hypotheses by observing the quantity of water formed when there is equilibrium.

But if the water is absorbed as soon as it is formed, and a steady stream of oxygen and hydrogen flows into the vessel where combination takes place at such a rate as to keep the pressure there constant, and if v molecules of hydrogen flow into this vessel per unit time, then we have on the first hypothesis, since v molecules of water must be absorbed in unit time,

$$v = \frac{np}{\tau_2},$$

and

$$\frac{v}{2} = \frac{p^2}{\tau_4} - \frac{q}{t_2};$$

$$\therefore \quad v^2 = \frac{\tau_4}{\tau_2{}^2} n^2 \left(\frac{v}{2} + \frac{q}{t} \right). \quad . \quad . \quad . \quad . \quad (19)$$

We know n and q, for they are the number of molecules of hydrogen and oxygen respectively in the vessel where combination takes place, and we may suppose t_2 determined by observations on oxygen alone.

On the second hypothesis the equations are

$$v = \frac{m^2 p}{\tau_3},$$

$$v = \frac{m^2}{\tau_1} - \frac{n}{t_1},$$

$$\tfrac{1}{2} v = \frac{p^2}{\tau_4} - \frac{q}{t_2};$$

hence we see that

$$v^2 = \frac{\tau_1{}^2 \tau_4}{\tau_3{}^2} \left(v + \frac{n}{t_1} \right)^2 \left(\tfrac{1}{2} v + \frac{q}{t_2} \right). \quad . \quad . \quad . \quad (20)$$

This equation is not the same as the previous one; we may suppose that t_1 has been found by experiments on hydrogen alone. So that by making experiments in the way we have described, and measuring the rate at which hydrogen and oxygen must flow into the vessel where the combination takes place so as to keep the pressure there constant, we could determine whether equation (19) or (20) agreed best with the results of the experiments, and in this way determine which is the right hypothesis.

The case we have just considered includes also the theory

of the formation of ozone, if we suppose that the molecule of ozone consists of three atoms of oxygen. We may prove, in the same way as before, that if v be the number of ozone molecules and N the total number of oxygen atoms, whether free or in oxygen molecules or in ozone, that

$$v^2 = \tfrac{1}{8}\frac{t_3{}^2 \tau_4}{t_2 \tau_2{}^2}(N - 3v)^3 \quad . \quad . \quad . \quad (21)$$

if we adopt the first hypothesis, and that

$$v^2 = \tfrac{1}{8}\frac{t'_3{}^2 \tau_4{}^3}{t_2{}^3 \tau_3{}^2}(N - 3v)^3 \quad . \quad . \quad . \quad (22)$$

if we adopt the second.

These equations are of exactly the same type, and according to both of them the proportion of ozone formed ought to increase with the density of the oxygen from which it is formed. I am not aware whether this has been observed or not. The decomposition of steam by the silent electrical discharge would be a very suitable case for comparing the theory given in this paragraph with experiment; but though the decomposition has been observed, no quantitative experiments seem to have been made on this subject. In fact no such experiments seem to have been made on the combination of any dyad element with a monad.

§ 5. We will now go on to investigate the following case which occurs frequently in chemical investigations. Three monovalent gases A, B, C are mixed together in a closed vessel. A can combine with both B and C to form the compounds AB, AC respectively; but B and C cannot combine. We wish to find how much of each compound is formed.

Let m = the number of atoms of A in the vessel.
n = the number of molecules of A.
p = the number of atoms of B.
q = the number of molecules of B.
r = the number of atoms of C.
s = the number of molecules of C.
u = the number of molecules of the compound (AB).
v = the number of molecules of the compound (AC).
M = the total number of atoms of A in the vessel, whether free or in molecules, or in the compounds AB and AC.
N = the total number of atoms of B, whether free or in molecules of B, or in the molecules of (AB).
P = the total number of atoms of C, whether free or in molecules of C, or in molecules of (AC).

t_1 = the time two atoms stay together in the molecule of A.

t_2 = the time two atoms stay together in the molecule of B.

t_3 = the time two atoms stay together in the molecule of C.

t_4 = the time an atom of A stays with an atom of B in the molecule of AB.

t_5 = the time an atom of A stays with an atom of C in the molecule of AC.

$\dfrac{\tau_1}{m}$ = the time an atom of A is free from another atom of the same substance.

$\dfrac{\tau_2}{p}$ = the time an atom of A is free from an atom of B.

$\dfrac{\tau_3}{r}$ = the time an atom of A is free from an atom of C.

$\dfrac{\tau_4}{p}$ = the time an atom of B is free from another atom of the same substance.

$\dfrac{\tau_5}{r}$ = the time an atom of C is free from another atom of the same substance.

Then, by the same reasoning as before, we have

$$
\left.
\begin{aligned}
\frac{dm}{dt} &= \frac{2n}{t_1} + \frac{u}{t_4} + \frac{v}{t_5} - \frac{2m^2}{\tau_1} - \frac{mp}{\tau_2} - \frac{mr}{\tau_3} \\
\frac{dn}{dt} &= \frac{m^2}{\tau_1} - \frac{n}{t_1} \\
\frac{dp}{dt} &= \frac{2q}{t_2} + \frac{u}{t_4} - \frac{2p^2}{\tau_4} - \frac{mp}{\tau_2} \\
\frac{dq}{dt} &= \frac{p^2}{\tau_4} - \frac{q}{t_2} \\
\frac{dr}{dt} &= \frac{2s}{t_3} + \frac{v}{t_5} - \frac{2r^2}{\tau_5} - \frac{mr}{\tau_3} \\
\frac{ds}{dt} &= \frac{r^2}{\tau_5} - \frac{s}{t_3} \\
\frac{du}{dt} &= \frac{mp}{\tau_2} - \frac{u}{t_4} \\
\frac{dv}{dt} &= \frac{mr}{\tau_3} - \frac{v}{t_5}
\end{aligned}
\right\} \qquad . \quad . \ (23)
$$

Let us suppose that things have got into a state of equilibrium, then the differential coefficients of all the quantities with respect to the time will vanish, so that these equations may now be written

$$\left.\begin{aligned}
\frac{m^2}{\tau_1} &= \frac{n}{t_1}; \quad \frac{p^2}{\tau_4} = \frac{q}{t_2} \\
\frac{r^2}{\tau_5} &= \frac{s}{t_3}; \quad \frac{mp}{\tau_2} = \frac{u}{t_4}
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\frac{mr}{\tau_3} = \frac{v}{t_5};$$

so that

$$\left.\begin{aligned}
u^2 &= \frac{t_4^2}{\tau_2^2} \frac{\tau_1}{t_1} \frac{\tau_4}{t_2} nq; \text{ or say } u^2 = \alpha nq \\
v^2 &= \frac{t_5^2}{\tau_3^2} \frac{\tau_1}{t_1} \frac{\tau_5}{t_3} nr; \text{ or say } v^2 = \beta nr
\end{aligned}\right\} \quad . \quad . \quad (25)$$

Now the number of free atoms will in all practical cases be very small compared with the number of molecules, so that m, p, r are very small compared with n, q, s respectively, so that we may put

$$n = \tfrac{1}{2} (M - u - v)$$
$$q = \tfrac{1}{2} (N - u)$$
$$s = \tfrac{1}{2} (P - v).$$

So that equations (25) become

$$u^2 = \tfrac{1}{4} \alpha (M - u - v)(N - u),$$
$$v^2 = \tfrac{1}{4} \beta (M - u - v)(P - v),$$

two equations to determine u and v. If we put $M = N = P$ we have two equations for u/M, v/M, the coefficients of which do not involve M; so that unless α and β are functions of the density the same proportion of the gases will enter into combination at all pressures. We see from equation (25) that the number of molecules of the compound AB is proportional to the geometric mean of the number of free molecules of A and B, and similarly that the number of molecules of the compound AC is proportional to the geometric mean of the number of free molecules of A and C. If we look at the value of α we see, by comparing it with the results given in § 3, that it can be determined by experiments on the combination of A and B by themselves. Thus from the experiments of M. Lemoine we see that for hydrogen and iodine

$a = 40.1$, so that whenever hydrogen and iodine are mixed with some monovalent substance which combines with the hydrogen, but not with the iodine, the number of molecules of hydriodic acid is about 6.2 times the geometric mean of the numbers of the free hydrogen and iodine molecules, and, generally, equations (25) show that in all cases of combination of this kind the number of molecules of the compound AB bears to the geometric mean of the numbers of free molecules of A and B a ratio which is independent of the nature of the substance C, and similarly the number of AC molecules bears to the geometric mean of the numbers of the uncombined A and C molecules a ratio which is independent of the nature of B.

§ 6. I have not been able to find any researches bearing on the kind of chemical combination considered in the last paragraph; but as the somewhat analogous combination which takes place when hydrogen, carbonic oxide, and oxygen are mixed together and then exploded has been studied by several chemists, we shall in this paragraph investigate theoretically the result of such combination, although the case is not one where we should expect to find a very close agreement between the calculated and the observed results, as so much heat is generated in the explosion that the temperature must vary greatly during the time combination is taking place, and thus complicate the question. We shall suppose that water is produced by the combination of a molecule of hydrogen with an atom of oxygen, and carbonic acid by the combination of a molecule of carbonic oxide with an atom of oxygen; we shall also suppose that the hydrogen does not combine with the carbonic oxide.

Let m = the number of hydrogen molecules.

n = the number of oxygen atoms.

p = the number of oxygen molecules.

r = the number of carbonic oxide molecules.

s = the number of water molecules.

u = the number of carbonic acid molecules.

t_1 = the time two hydrogen atoms remain together in the hydrogen molecule.

t_2 = the time two oxygen molecules remain together in the oxygen molecule.

t_3 = the time an oxygen atom stays with a hydrogen molecule in the water molecule.

t_4 = the time an oxygen atom stays with a carbonic oxide molecule in the molecule of carbonic acid.

$\dfrac{\tau_1}{n}$ = the time an oxygen atom remains free from another oxygen atom.

$\dfrac{\tau_2}{m}$ = the time an oxygen atom remains free from a hydrogen molecule.

$\dfrac{\tau_3}{r}$ = the time an oxygen atom remains free from a carbonic oxide molecule.

M = the total number of hydrogen molecules, whether free or in the water molecule.

N = the total number of oxygen atoms, whether free or in oxygen molecules, or in water, or carbonic acid molecules, but not counting the oxygen atoms in the carbonic oxide molecule.

P = the total number of carbonic oxide molecules, whether free or in the carbonic acid molecule.

Then, by the same reasoning as before, we get the following equations :—

$$
\left.
\begin{aligned}
m + s &= \text{M} \\
n + 2p + s + u &= \text{N} \\
r + u &= \text{P} \\
\frac{dp}{dt} &= \frac{n^2}{\tau_1} - \frac{p}{t_2} \\
\frac{ds}{dt} &= \frac{nm}{\tau_2} - \frac{s}{t_3} \\
\frac{du}{dt} &= \frac{nr}{\tau_3} - \frac{u}{t_4}
\end{aligned}
\right\} ; \quad . \quad . \quad . \quad . \quad (26)
$$

when things are in equilibrium $\dfrac{dp}{dt}, \dfrac{ds}{dt}, \dfrac{du}{dt}$ are all zero ; so that

$$
\frac{n^2}{\tau_1} = \frac{p}{t_2},
$$

$$
\frac{nm}{\tau_2} = \frac{s}{t_3},
$$

$$
\frac{nr}{\tau_3} = \frac{u}{t_4} ;
$$

hence

$$s^2 = \frac{t_3{}^2}{\tau_2{}^2} \frac{\tau_1}{t_2} pm^2 \left.\begin{array}{c} \\ \\ \\ \\ \end{array}\right\} \quad . \quad . \quad . \quad . \quad (27)$$

$$u^2 = \frac{t_4{}^2}{\tau_3{}^2} \frac{\tau_1}{t_2} pr^2$$

or substituting for p, m, r their values from (26), and supposing that the number of free oxygen atoms is small compared with the number of molecules of any kind,

$$s^2 = \tfrac{1}{2} \frac{t_3{}^2}{\tau_2{}^2} \frac{\tau_1}{t_2} (N - s - u)(M - s)^2 \left.\begin{array}{c} \\ \\ \\ \\ \end{array}\right\} \quad . \quad . \quad (28)$$

$$u^2 = \tfrac{1}{2} \frac{t_4{}^2}{\tau_3{}^2} \frac{\tau_1}{t_2} (N - s - u)(P - u)^2$$

These two equations are sufficient to determine s and u, and we see that, since the right-hand side of the equations contains cubes of the number of molecules, while the left-hand side only contains squares, the combination will be relatively greater at high than at low pressures, at any rate when the quantity of the gases which combine is small compared with the quantity of them which is left free.

From equations (27) we see that

$$s/u = \frac{t_3}{t_4} \frac{\tau_3}{\tau_2} m/r,$$

so that the ratio of the quantity of water formed to the quantity of carbonic acid always bears a constant ratio to the ratio of quantity of hydrogen left free to the quantity of free carbonic oxide. The following account of Horstmann's experiments on this reaction from Watts's 'Dictionary of Chemistry,' 3rd Supplement, p. 433, is of interest in connection with this result :—

" The law according to which the oxygen is divided between the combustible gases may be expressed thus :—The proportion of the resulting water-vapour to the resulting carbon dioxide is equal to the proportion of the unburnt hydrogen to the unburnt carbon oxide, multiplied by a coefficient of affinity which is independent of the proportion of the combustible gases, but varies with the relative quantities of oxygen added. This coefficient of affinity varies, according to Horstmann, between 4·0 and 6·4 when between 20 and 70 per cent. of the combustible gases is burnt, the maximum coefficient coinciding with the combustion of 30–40 per cent. of the

gases. In other words, the proportion of water-vapour to carbon dioxide was found to be from 4·0 to 6·4 times as great as the proportion of hydrogen to carbon oxide in the residue unburnt. Hence relatively more hydrogen than carbon oxide is burnt in all cases ; the affinity of oxygen for hydrogen is greater than for carbon oxide.

" The variability in the coefficient of affinity is due to the circumstance that the physical conditions of the reaction vary with the relative quantities of oxygen present. With equal quantities of oxygen the coefficient remains constant, not only when the proportion of hydrogen to carbonic oxide is altered, but also when the unconsumed portion of the combustible gases is replaced partially or entirely by an indifferent gas of similar physical character, such as nitrogen, although the proportion of unburnt gases to products of combustion varies in both cases."

§ 7. The next case we shall consider is when three atoms of one element A unite with one of another element B to form the compound which we shall denote by A_3B. This case is more complicated than any of the previous ones when the combination could always be supposed to take place by an atom or molecule of one substance uniting with an atom of another. We may make several hypotheses about the way in which the compound A_3B may be formed.

1. We may suppose that there is, in addition to free atoms and molecules of A, a very small number of triplets; this number may be supposed to be very small compared with the number of molecules or even of free atoms of A. We may then suppose that the molecule of the compound A_3B is formed by one of those triplets combining with an atom of B.

2. We may suppose that the molecule of A_3B is formed by an atom and a molecule of A meeting simultaneously with each other and with an atom of B.

3. We may suppose that three free atoms of A meet simultaneously with each other and with an atom of B.

We shall investigate the consequences of each of these hypotheses. Let us begin with the first hypothesis.

Let m = the number of atoms of A.
   n = the number of molecules of A.
   p = the number of triplets of A.
   q = the number of atoms of B.
   r = the number of molecules of B.
   s = the number of molecules of the compound A_3B.

M = the total number of A atoms, whether free, in molecules, in triplets, or in molecules of A_3B.

N = the total number of B atoms.

t_1 = the time the atoms in the A molecule stay together.

t_2 = the time the atoms in the A triplets stay together.

t_3 = the time the atoms in the B molecule stay together.

t_4 = the time the triplet A_3 stays with the atom of B in the molecule of A_3B.

$\dfrac{\tau_1}{m}$ = the time an atom of A is free from one other atom of A.

$\dfrac{\tau_2}{n}$ = the time an atom of A is free from a molecule of A.

$\dfrac{\tau_3}{q}$ = the time a triplet of A is free from an atom of B.

$\dfrac{\tau_4}{q}$ = the time one atom of B is free from another atom of the same.

Then if we suppose that when the molecule of A_3B is decomposed it splits up into the triplet A_3 and the atom B, and that when a triplet of A is decomposed it splits up into an atom and a molecule of A, we get the following equations:—

$$\left.\begin{aligned}
\frac{dm}{dt} &= \frac{2n}{t_1} + \frac{p}{t_2} - \frac{2m^2}{\tau_1} - \frac{mn}{\tau_2}\\[1mm]
\frac{dn}{dt} &= \frac{m^2}{\tau_1} + \frac{p}{t_2} - \frac{n}{t_1} - \frac{mn}{\tau_2}\\[1mm]
\frac{dp}{dt} &= \frac{mn}{\tau_2} + \frac{s}{t_4} - \frac{p}{t_2} - \frac{pq}{\tau_3}\\[1mm]
\frac{dq}{dt} &= \frac{2r}{t_3} + \frac{s}{t_4} - \frac{2q^2}{\tau_4} - \frac{pq}{\tau_3}\\[1mm]
\frac{dr}{dt} &= \frac{q^2}{\tau_4} - \frac{r}{t_3}\\[1mm]
\frac{ds}{dt} &= \frac{pq}{\tau_3} - \frac{s}{t_4}
\end{aligned}\right\} \quad . \quad . \quad . \quad (29)$$

$$m + 2n + 3p + 3s = M,$$
$$q + 2r + s = N.$$

When things have got into a condition of equilibrium we have

$$\left.\begin{aligned}
\frac{m^2}{\tau_1} &= \frac{n}{t_1} \\
\frac{mn}{\tau_2} &= \frac{p}{t_2} \\
\frac{q^2}{\tau_4} &= \frac{r}{t_3} \\
\frac{pq}{\tau_3} &= \frac{s}{t_4}
\end{aligned}\right\} ; \quad \cdots \cdots \quad (30)$$

so that

$$s^2 = \frac{t_4{}^2 \tau_4 t_2{}^2 \tau_1}{\tau_3{}^2 t_3 \tau_2{}^2 t_1} n^3 r, \text{ say} = \alpha n^3 r. \quad \cdots \quad (31)$$

Or, as the numbers of free atoms and triplets are small compared with the numbers of molecules, we may write this equation as

$$s^2 = \tfrac{1}{16}\alpha(M - 3s)^3(N - s). \quad \cdots \cdots \quad (32)$$

We see from the form of this equation that the combination will be relatively greater at high than at low pressures. We may express this equation in words by saying that the ratio of the number of molecules of A_3B to the number of free molecules of A is equal to the geometric mean of the number of free molecules of A and B multiplied by a constant.

The most prominent case of combination of this kind is that of the formation of ammonia when the silent electrical discharge is allowed to pass through a mixture of hydrogen and nitrogen. The formation of triplets of hydrogen atoms in this case seems not unlikely, as triplets of oxygen atoms would be formed under the same circumstances. The existence of ozone is detected by its possessing the properties of oxygen in an exaggerated degree, so that it is possible that if the properties of oxygen had not been so marked the existence of ozone might have been overlooked.

Let us now go on to discuss the second hypothesis.

Let the notation be the same as before, with the addition that $\dfrac{\tau_5}{nq}$ = the time that elapses before an atom of A unites with a molecule of A and an atom of B simultaneously.

Then if we suppose that a molecule of A_3B breaks up into an atom and a molecule of A and a molecule of B, and that

triplets of A do not exist, we have the following equations:—

$$
\left.\begin{array}{l}
\dfrac{dm}{dt} = \dfrac{2n}{t_1} + \dfrac{s}{t_4} - \dfrac{2m^2}{\tau_1} - \dfrac{mnq}{\tau_5} \\[2ex]
\dfrac{dn}{dt} = \dfrac{m^2}{\tau_1} + \dfrac{s}{t_4} - \dfrac{n}{t_1} - \dfrac{mnq}{\tau_5} \\[2ex]
\dfrac{dq}{dt} = \dfrac{2r}{t_3} + \dfrac{s}{t_4} - \dfrac{2q^2}{\tau_4} - \dfrac{mnq}{\tau_5} \\[2ex]
\dfrac{dr}{dt} = \dfrac{q^2}{\tau_4} - \dfrac{r}{t_3} \\[2ex]
\dfrac{ds}{dt} = \dfrac{mnq}{\tau_5} - \dfrac{s}{t_4}
\end{array}\right\} \quad \cdot \quad \cdot \quad (33)
$$

When things have got into a steady state, we have

$$
\left.\begin{array}{l}
\dfrac{m^2}{\tau_1} = \dfrac{n}{t_1} \\[2ex]
\dfrac{q^2}{\tau_4} = \dfrac{r}{t_3} \\[2ex]
\dfrac{mnq}{\tau_5} = \dfrac{s}{t_4}
\end{array}\right\} ; \quad \cdots \cdots \quad (34)
$$

$$
\therefore \; s^2 = \dfrac{t_4{}^2 \tau_1 \tau_4}{\tau_5{}^2 t_1 t_3} r n^3, \quad \cdots \cdots \quad (35)
$$

a formula of exactly the same form as the one obtained on the first hypothesis, so that the equilibrium state is the same whichever hypothesis we adopt.

If we take the third hypothesis, and use the same notation as before, with the addition that

$$
\dfrac{\tau_6}{m^2 q} =
$$ the time that elapses before a free atom of A unites with two free atoms of A and an atom of B simultaneously,

this quantity is evidently inversely proportional to $m^2 q$, as $m^2 q$ is the number of groups, if m and q be large, which can be formed of two A atoms and one B atom. If we suppose that there are no triplets, and that the molecules of A_3B when decomposed split up into three atoms of A and one of B, we have the following equations :—

$$\left.\begin{aligned}
\frac{dm}{dt} &= \frac{2n}{t_1} + \frac{3s}{t_4} - \frac{2m^2}{\tau_1} - \frac{3m^3q}{\tau_6} \\
\frac{dn}{dt} &= \frac{m^2}{\tau_1} - \frac{n}{t_1} \\
\frac{dq}{dt} &= \frac{2r}{t_3} + \frac{s}{t_4} - \frac{2q^2}{\tau_4} - \frac{m^3q}{\tau_6} \\
\frac{dr}{dt} &= \frac{q^2}{\tau_4} - \frac{r}{t_3} \\
\frac{ds}{dt} &= \frac{m^3q}{\tau_6} - \frac{s}{t_4}
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (36)$$

When things are in a steady state these equations become

$$\left.\begin{aligned}
\frac{m_2}{\tau_1} &= \frac{n}{t_1} \\
\frac{q_2}{\tau_4} &= \frac{r}{t_3} \\
\frac{m^3q}{\tau_6} &= \frac{s}{t_4}
\end{aligned}\right\} ; \quad . \quad . \quad . \quad . \quad . \quad (37)$$

so that

$$s^2 = \frac{t_4^2 \tau_1^3 \tau_4}{\tau_6^2 t_1^3 t_3} r n^3. \quad . \quad . \quad . \quad (38)$$

This formula is of the same form as those given by the first and second hypotheses, so that all three lead to the same results when there is chemical equilibrium.

We might apply similar principles to any case of gaseous combination; but after what has been given the reader will, I think, have no difficulty in forming for himself the equations which hold for any particular case. In conclusion, I may say that much of the reasoning would seem to be applicable to liquids, and we should expect many of the formulæ to be approximately true for the combination of liquids as well as of gases, though we know so little about the molecular composition of liquids that it is difficult to base the reasoning in this case on direct dynamical principles.

XXXIII. *On the Cause of Mild Polar Climates.*
By James Croll, *LL.D., F.R.S.*[*]

THERE are few facts within the domain of geology better established than that at frequent periods in the past the polar regions enjoyed a comparatively mild and equable climate, and that places now buried under permanent snow and ice were then covered with a rich and luxuriant vegetation. Various theories have been advanced to account for this remarkable state of things, such as a different distribution of sea and land, a change in the obliquity of the ecliptic, a displacement in the position of the earth's axis of rotation, and so forth. The true explanation will, I feel persuaded, be found to be the one I gave many years ago. The steps by which the results were reached were as follows :—

The annual quantity of heat received from the sun at the equator is to that at the poles as 12 to 4·98, or, say, as 12 to 5. This is on the supposition that the same percentage of rays is cut off by the atmosphere at the equator as at the poles, which, of course, is not the case. More is cut off at the poles than at the equator, and consequently the difference in the amount of heat received at the two places is actually greater than that indicated by the ratio 12 to 5. But, assuming 12 to 5 to be the ratio, the question arose what ought to be the *difference* of temperature between the two places in question on the supposition that the temperature was due solely to the direct heat received from the sun ? This was a question difficult to answer, for its answer mainly depended upon two things, regarding both of which a very considerable amount of uncertainty prevailed.

First, it was necessary to know how much of the total amount of heat received by the earth was derived from the sun and how much from the stars and other sources, or, in other words, from space. Absolute zero is considered to be 461° below zero Fahr. The temperature of the equator is about 80°. This gives 541° as the absolute temperature of the equator. Now were all the heat received by the earth derived simply from the sun, and were the temperature of each place proportionate to the amount directly received, then the absolute temperature of the poles would be $\frac{5}{12}$ of that of the equator, or 225°. This would give a difference of 316° between the temperature of the equator and that of the poles. According to Pouillet and Herschel, space has a temperature of −239°, or 222° of absolute temperature. If this be

the temperature of space, then only 319° of the absolute temperature of the equator are derived from the sun ; consequently as the poles receive from the sun only $\frac{5}{12}$ of this amount of temperature, or 133°, this will give merely 186° as the difference which ought to exist between the equator and the poles. There is, however, good reason for believing that the temperature of space is far less than that assigned by Pouillet and Herschel—that, in fact, it is probably not far above absolute zero. Therefore by adopting so high a temperature as −239° we make the difference between the temperature of the equator and that of the poles too small.

Second, it was necessary to know at what rate the temperature increased or decreased with a given increase or decrease in the amount of heat received. It was well known that Newton's law—that the change of temperature was directly proportionate to the change in the quantity of heat received—was far from being correct. The formula of Dulong and Petit was found to give results pretty accurate within ordinary limits of temperature. But it would not have done, in making my estimate, to take that formula, if I adopted Herschel's estimate of the temperature of space ; for it would have made the difference of temperature between the equator and the poles by far too small. Newton's law, if we adopt Herschel's estimate of the temperature of space, would give results much nearer the truth ; for the error of the one would, to a large extent at least, neutralize that of the other.

From such uncertain data it was, of course, impossible to arrive at results which could in any way be regarded as accurate. But it so happens that perfect accuracy of results in the present case was not essential : all that really was required was a rough estimate of what the difference of temperature between the equator and the poles ought to be. The method adopted showed pretty clearly, however, that the difference of temperature could not be less (although probably more) than 200° ; but the present actual difference does not probably exceed 80°. We have no means of ascertaining with certainty what the mean annual temperature of the poles is ; but as the temperature of lat. 80° N. is 4°·5, that of the poles is probably not under 0°. If the present difference be 80°, it is then 120° less than it would be did the temperature of each place depend alone on the heat received directly from the sun. This great reduction from about 200° to 80° can, of course, be due to no other cause than to a transference of heat from the equator to the poles. The question then arose, by what means was this transference effected ? There were only two agencies available—the transference must be effected either by aerial or by

ocean-currents. It was shown at considerable length ('Climate and Time,' pp. 27–30, and other places) that the amount of heat that can be conveyed from the equator to the poles by means of aerial currents is trifling, and that, consequently, the transference must be referred to the currents of the ocean. It became obvious then that the influence of ocean-currents in the distribution of heat over the globe had been enormously underestimated. In order to ascertain with greater certainty that such had been the case, I resolved on determining, if possible, in absolute measure the amount of heat actually being conveyed from the equator to temperate and polar regions by means of ocean-currents.

The only great current whose volume and temperature had been ascertained with any degree of certainty was the Gulf-stream. On computing the absolute amount of heat conveyed by that stream, it was found to be more than equal to all the heat received from the sun within 32 miles on each side of the equator. The amount of equatorial heat carried into temperate and polar regions by this stream alone is therefore equal to one fourth of all the heat received from the sun by the North Atlantic from the Tropic of Cancer up to the Arctic circle[*]. Although the heating-power of the Gulf-stream had long been known, yet no one had imagined that the warmth of our climate was due, to such an enormous extent, to the heat conveyed by that stream. The amount of heat received by an equatorial zone 64 miles in breadth represents, be it observed, merely the amount conveyed by one current alone. There are several other great currents some of which convey as much heat polewards as the Gulf-stream. On taking into account the influence of the whole system of oceanic circulation, it was not surprising that the difference of temperature between the equator and the poles should be reduced from 200° to 80°.

From these considerations, the real cause of former comparatively mild climates in Arctic regions became now apparent. All that was necessary to confer on, say, Greenland a condition of climate which would admit of the growth of a luxuriant vegetation was simply an increase in the amount of heat transferred from equatorial to Arctic regions by means of ocean-currents. And to effect this change of climate no very great amount of increase was really required; for it was shown that the severity of the climate of that region was about as much due to the cooling effect of the permanent snow and ice as to an actual want of heat. An increase in the amount of warm water entering the Arctic Ocean, just suffi-

* 'Climate and Time,' pp. 34, 35; Phil. Mag., February 1870.

cient to prevent the formation of permanent ice, was all that was really necessary ; for were it not for the presence of ice the summers of Greenland would be as warm as those of England.

Were the whole of the warm water of the Gulf-stream at present to flow into the Arctic Ocean, it would probably remove the ice of Greenland. Any physical changes, such as those that have been discussed on former occasions, which would greatly increase the volume and temperature of the stream and deflect more of its waters into the Arctic Ocean would, there is little doubt, confer on the polar regions a climate suitable for plant and animal life. At present the Gulf-stream bifurcates in mid-Atlantic, one branch passing north-eastwards into the Arctic regions, whilst the larger branch turns south-eastwards by the Azores, and after passing the Canaries reenters the equatorial current. As the Gulf-stream, like other great currents of the ocean, follows almost exactly the path of the prevailing winds *, it bifurcates in mid-Atlantic simply because the winds blowing over it bifurcate also. Any physical change which would prevent this bifurcation of the winds and cause them to blow north-eastwards would probably impel the whole of the Gulf-stream waters into the Arctic seas. All this doubtless might quite well be effected without any geographical changes, although changes in the physical geography of the North Atlantic might be helpful.

These considerations regarding the influence of the Gulf-stream point to another result of an opposite character. It is this : if a large *increase* in the volume and temperature of the stream would confer on Greenland and the Arctic regions a condition of climate somewhat like that of North-western Europe, it is obvious, as has been shown at length on former occasions, that a large *decrease* in its temperature and volume would, on the other hand, lead to a state of things in North-western Europe approaching to that which now prevails in Greenland. A decrease leads to a glacial, an increase to an interglacial condition of things.

Sir William Thomson on Mild Arctic Climates.—In a paper read before the Geological Society of Glasgow in February 1877, Sir William maintains also that an increase in the amount of heat conveyed by ocean-currents to the Arctic regions, combined with the effect of Clouds, Wind, and Aqueous Vapour, is perfectly sufficient to account for the warm and temperate condition of climate which is known to

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* See 'Climate and Time,' p. 213.

have prevailed in those regions during former epochs.   The
following quotations will show Sir William's views :—

" A thousand feet of depression would submerge the continents
of Europe, Asia, and America, for thousands of miles from their
present northern coast-lines ; and would give instead of the present
land-locked, and therefore ice-bound Arctic sea, an open iceless
ocean, with only a number of small steep islands to obstruct the
free interchange of water between the North Pole and temperate
or tropical regions.   That the Arctic sea would, in such circum-
stances, be free from ice quite up to the north pole may be, I think,
securely inferred from what, in the present condition of the globe,
we know of ice-bound and open seas in the northern hemisphere
and of the southern ocean abounding in icebergs, but probably
nowhere ice-bound up to the very coast of the circumpolar Ant-
arctic continent, except in more or less land-locked bays. . . . . .
" Suppose now the sea, unobstructed by land from either pole to
temperate or tropical regions, to be iceless at any time, would it
continue iceless during the whole of the sunless polar winter ?
Yes, we may safely answer.   Supposing the depth of the sea to be
not less than 50 or 100 fathoms, and judging from what we know
for certain of ocean-currents, we may safely say that differences of
specific gravity of the water produced by difference of temperature
not reaching anywhere down to the freezing-point would cause
enough of circulation of water between the polar and temperate or
tropical regions to supply all the heat radiated from the water
within the Arctic circle during the sunless winter, if air contri-
buted none of it.   Just think of a current of three quarters of a
nautical mile per hour, or 70 miles per four days, flowing towards
the pole across the Arctic circle.   The area of the Arctic circle is
700 square miles for each mile of its circumference.   Hence 40
fathoms deep of such a current would carry in, per twenty-four
hours, a little more than water enough to cover the whole area to
a depth of 1 fathom ; and this, if $7°\cdot1$ Cent. above the freezing-
point, would bring in just enough of heat to prevent freezing, if in
twenty-four hours as much heat were radiated away as taken from
a tenth of a fathom of ice-cold water would leave it ice at the
freezing-point.   This is no doubt much more than the actual
amount of radiation, and the supposed current is probably much
less than it would be if the water were ice-cold at the pole and
$7°$ Cent. at the Arctic circle.   Hence, without any assistance from
air, we find in the convection of heat by water alone a sufficiently
powerful influence to prevent any freezing-up in polar regions at
any time of year."   (Trans. of the Geol. Soc. of Glasgow, 22nd
February, 1877.)

That an amount of warm water flowing into the Arctic
Ocean equal to that assumed by Sir William Thomson, along
with the effects of clouds, wind, dew, and other agencies to
which he refers, would wholly prevent the existence of per-

manent ice in those regions, is a conclusion which, I think, can hardly be doubted. It is with the greatest deference that I venture to differ from so eminent a physicist; but I am unable to believe that such a transference of water from intertropical and temperate regions could be effected by the agency to which he attributes it. Certainly the amount of heat conveyed by means of a circulation resulting from difference of specific gravity, produced by difference of temperature, must be trifling when compared with that of ocean-currents produced by the impelling force of the winds. Take, for example, the case of the Gulf-stream. If the amount of heat conveyed from intertropical regions into the North Atlantic by means of difference of density resulting from difference of temperature were equal to that conveyed by the Gulf-stream, it would follow, as has been proved [*], that the Atlantic would be far warmer in temperate and arctic than in intertropical regions. Taking the annual quantity of heat received from the sun per unit surface at the equator as 1000, the quantities received by the three zones would be respectively as follows :—

Equator 1000
Torrid zone 975
Temperate zone . . . 757
Frigid zone 454

Assume, then, that as much heat is conveyed from intertropical regions into the Atlantic and Arctic seas by this circulation from difference of specific gravity as by the Gulf-stream, and assume also that one half of the total heat conveyed by the two systems of circulation goes to warm the Arctic Ocean, and the other half remains in temperate regions, the following would then be the relative quantities of heat possessed by the three zones :—

Atlantic in torrid zone . . . 671
,, in temperate zone . . 940
,, in frigid zone . . . 766

There is a still more formidable objection to the theory. It has been demonstrated, from the temperature-soundings made by the 'Challenger' Expedition [†], that the general surface of the North Atlantic must, in order to produce equilibrium, stand at a higher level than at the equator : in other words,

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[*] 'Climate and Time,' Chap. xi. ; Phil. Mag., March 1874.
[†] 'Climate and Time,' pp. 220–225 ; Phil. Mag., September and December 1875 ; 'Nature,' November 25th, 1875.

the surface of the Atlantic is lowest at the equator, and rises with a gentle slope to well nigh the latitude of England. This curious condition of things is owing to the fact that, in consequence of the enormous quantity of warm water from intertropical regions which is being continually carried by the Gulf-stream into temperate regions, the mean temperature of the Atlantic water, considered from its surface to the bottom, is greater, and the specific gravity less, in temperate regions than at the equator. In consequence of this difference of specific gravity, the surface of the Atlantic at latitude 23° N. must stand 2 feet 3 inches above the level of the equator, and at latitude 38° N. 3 feet 3 inches above the equator. In this case it is absolutely impossible that there can be a flow in the Atlantic from the equatorial to the temperate regions resulting from difference of specific gravity. If there is any motion of the water from that cause, it must, in so far as the Atlantic is concerned, be in the opposite direction, viz. from the temperate to the equatorial regions.

All, or almost all, the heat which the Arctic seas receive from intertropical regions in the form of warm water comes from the Atlantic, and not from the Pacific; for the amount of warm water entering by Behring Strait must be comparatively small. It therefore follows from the foregoing considerations that none of that equatorial heat can be conveyed by a circulation resulting from difference of specific gravity produced by difference of temperature.

It is assumed as a condition in this theory that a submergence of the Arctic land of several hundred feet must have taken place in order to convert that land into a series of islands allowing of the free passage of water round them. But the evidence of Geology, as was shown on a former occasion[*], is not altogether favourable to the idea that those warm climates were in any way the result of a submergence of the polar land. Take the Miocene epoch as an example: all the way from Ireland and the Western Isles, by the Faroes, Iceland, Franz-Joseph Land, to North Greenland, the Miocene vegetation and the denuded fragmentary state of the strata point to a much wider distribution of Polar land than that which now obtains in those regions.

Mr. Alfred R. Wallace on Mild Arctic Climates.—The theory that the mild climates of Arctic regions were due to an inflow of warm water from intertropical and temperate regions has also been fully adopted by Mr. Alfred R. Wallace. But, unlike Sir William Thomson, he does not attribute this

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[*] Geol. Mag., September 1878.

transference of warm water to a circulation resulting from difference of density produced by difference of temperature, but to currents caused by the impelling force of the wind.

Mr. Wallace shares in the opinion, now entertained by a vast number of geologists, that during the whole of the Tertiary period the climate of the north temperate and polar regions was uniformly warm and mild, without a trace of any intervening epochs of cold. According to him there were no glacial or interglacial periods during Tertiary times. In this case he, of course, does not suppose that the inflow of warm water into Arctic regions, on which the mild condition of climate depended, was in any way due to those physical agencies which came into operation during an interglacial period. Mr. Wallace accounts for the mild Arctic climate during the Tertiary period by the supposition that at that time there were probably several channels extending from equatorial to arctic regions through the eastern and western continents, allowing of a continuous flow of intertropical water into the Arctic Ocean. Mr. Wallace expresses his views on the point thus:—

"The distribution of the Eocene and Miocene formations shows that during a considerable portion of the Tertiary period an inland sea, more or less occupied by an archipelago of islands, extended across Central Europe between the Baltic and the Black and Caspian Seas, and thence by narrower channels south-eastward to the valley of the Euphrates and the Persian Gulf, thus opening a communication between the North Atlantic and the Indian Ocean. From the Caspian also a wide arm of the sea extended during some part of the Tertiary epoch northwards to the Arctic Ocean; and there is nothing to show that this sea may not have been in existence during the whole Tertiary period. Another channel probably existed over Egypt into the eastern basin of the Mediterranean and the Black Sea; while it is probable that there was a communication between the Baltic and the White Sea, leaving Scandinavia as an extensive island. Turning to India, we find that an arm of the sea of great width and depth extended from the Bay of Bengal to the mouths of the Indus; while the enormous depression indicated by the presence of marine fossils of Eocene age at a height of 16,500 feet in Western Tibet renders it not improbable that a more direct channel across Afghanistan may have opened a communication between the West-Asiatic and Polar seas." ('Island Life,' p. 184.)

My acquaintance with the Tertiary formations of the globe, and with the distribution of land and water during that period, is not such as to enable me to form any opinion whatever

either as to the probability or to the improbability of the existence of such channels as are assumed by Mr. Wallace. But, looking at the question from a physical point of view, it seems to me pretty evident that if such channels as he supposes existed, allowing of a continuous flow of equatorial water into the Arctic seas, it would certainly prevent the formation of permanent ice around the pole, and would doubtless confer on the arctic regions a mild and equable climate. This would be more particularly the case if, as Mr. Wallace supposes, owing to geographical conditions, far more of the equatorial water was deflected into the Arctic than into the Antarctic regions.

But at the same time I think it is just as evident that these channels would not neutralize the effects resulting from a high state of eccentricity. It may be quite true that the physical cause brought into operation during a high state of eccentricity might not be sufficient to reduce the quantity of warm water flowing into the Arctic Ocean to an extent that would permit of the formation of permanent ice around the pole, but it certainly would greatly diminish the flow into the Arctic Ocean. Supposing that at the commencement of the last glacial epoch the volume of the Gulf-stream was double what it is at present; this condition of things would not have prevented the operation of those physical agents which brought about the glacial epoch, although it, no doubt, would have considerably modified the severity of the glaciation resulting from their operation. The very same thing would hold true, though perhaps in a much greater degree, in reference to the channels assumed by Mr. Wallace.

If the emissive power of the sun was about the same during the Tertiary period as at present, and there is no good grounds for supposing it was otherwise, then the extra heat possessed by the northern temperate and arctic regions must have been derived either from the equatorial regions or from the southern hemisphere, or, what is more likely, from both. If so, then the temperature either of the southern hemisphere or of the intertropical regions, or both, must have been much lower during the Tertiary period than at the present day. A lowering of the temperature of the equatorial regions, resulting from this transference of heat, would tend to produce a more equable and uniform condition of climate over the whole of the northern hemisphere. As the area of the Arctic Ocean is small in comparison to that of the equatorial zone, from which the warm water was derived, the fall of temperature at the equator would be much less than the

rise at the pole. Supposing there had been a rise of, say, 30°
at the pole resulting from a fall of 10° at the equator (and this
is by no means an improbable assumption), this would reduce
the difference between the equator and the pole by 40°, or to
half its present amount. We should then have a climatic con-
dition pretty much resembling that which is known to have
prevailed during at least considerable portions of the Tertiary
period.

It is indeed very doubtful if such a climatic condition of
things as that could be brought about by a high state of eccen-
tricity with the present distribution of land and water ; but, on
the other hand, it is just as doubtful whether the channels of
communication assumed by Mr. Wallace could have brought
it about without the aid of eccentricity.

The very existence of so high a temperature on the northern
hemisphere during Tertiary times may be regarded as strong
presumptive proof that the geographical conditions obtaining
on the southern hemisphere were most unfavourable to the
flow of intertropical water into that hemisphere. This may
be one of the reasons why a high state of eccentricity failed
to produce a well-marked glacial epoch on the northern hemi-
sphere, the geographical conditions preventing a transference
of warm water into the southern hemisphere sufficient to pro-
duce true glaciation on the opposite hemisphere. That the
geographical conditions obtaining on the southern hemisphere
during Tertiary times were probably of such a character is an
opinion advanced by Mr. Wallace himself. " There are," he
says, " many peculiarities in the distribution of plants and of
some groups of animals in the southern hemisphere, which
render it almost certain that there has sometimes been a
greater extension of the antarctic lands during Tertiary times ;
and it is therefore not improbable that a more or less glaci-
ated condition may have been a long-persistent feature of
the southern hemisphere, due to the peculiar distribution of
land and sea, which favours the production of ice-fields and
glaciers " (p. 192).

Influences of Eccentricity during the Tertiary Period.—This
being the state of things on the southern hemisphere, the
glacial condition of the hemisphere, when its winter solstice
was in aphelion, would tend in a powerful manner to impel
the warm water of the south over on the northern hemisphere,
and thus raise its temperature. This, again, is a view which
has also been urged by Mr. Wallace. " Though high eccen-
tricity would," he remarks, " not directly modify the mild
climates produced by the state of the northern hemisphere
which prevailed during Cretaceous, Eocene, and Miocene

times *, it might indirectly affect it by increasing the mass
of antarctic ice, and thus increasing the force of the trade-
winds and the resulting northward-flowing warm currents.
. . . . And as we have seen that during the last three
million years the eccentricity has been almost always much
higher than it is now, we should expect that the quantity of
ice in the southern hemisphere will usually have been greater,
and will thus have tended to increase the force of those oceanic
currents which produce the mild climates of the northern
hemisphere " (p. 192).

There is little doubt but that the climate of the Tertiary
period was greatly affected by eccentricity; but, owing to the
difference in the geographical conditions of the two hemi-
spheres, eccentricity would exercise a much greater influence
on the climatic condition of the northern hemisphere when
the northern winter solstice was in perihelion than it would
do when it was in aphelion. Owing to the difference in
the conditions of the two hemispheres, the physical agents
brought into operation by a high state of eccentricity would
act more powerfully in impelling the equatorial waters
towards the Arctic regions when the winter solstice was in
perihelion than they would do in impelling the water towards
the Antarctic regions when the solstice was in aphelion. In
this case the northern hemisphere would be heated to a greater
extent when its winter solstice was in perihelion than it would
be cooled when the solstice was in aphelion. It is this cir-
cumstance which, I think, has misled geologists, and induced
them to conclude that because the physical agents brought
into operation when the winter solstice was in aphelion,
during a high state of eccentricity, failed to produce a well-
marked glacial epoch in Tertiary times, consequently the
climatic condition of that period was not much affected by
eccentricity.

It would seem to be owing to that peculiar difference be-
tween the conditions of the two hemispheres that, even during
high eccentricity, the physical agents in operation when the
winter solstice was in aphelion were unable to lower the tem-
perature of the northern hemisphere to an extent sufficient to
cover high temperate and arctic regions with permanent ice;
but for this very same reason these agents would be enabled
to raise the temperature to an extent exceptionally high when
the winter solstice was in perihelion. In other words, this
very combination of circumstances, which so much modified

* High eccentricity might not directly modify the mild climates, but
certainly the physical agents brought into operation by the high eccen-
tricity would do so.

the severity of what may be called the Tertiary cold periods, intensified to an exceptionally great extent the warmth and equability of what may be called the Tertiary warm periods.

Climate of the Tertiary Period, in so far as affected by Eccentricity.—If the foregoing conclusions are correct, the following would then seem to be the probable character of the climate of the Tertiary period, in so far as that climate was affected by eccentricity. As is truly remarked by Mr. Wallace, the eccentricity during the past three million years has been almost always much higher than it is now. It will consequently follow that very considerable portions of the Tertiary age would consist of alternate comparatively cold and exceedingly warm and equable periods. These may be said to correspond to the cold and warm periods of the glacial epoch; but, of course, they could in no sense be called glacial and interglacial periods; for the cold of the cold periods would not be such as to produce permanent ice, while the heat and equability of the warm periods would far exceed that of the interglacial periods.

Evidence of such Alternations of Climate.—That such oscillations occurred during the Tertiary period seems to be borne out by the facts of geology and palæontology. Mr. J. Starkie Gardner, a geologist who has had great experience in the fossil flora of the Tertiary deposits, says that such alternating warmer and colder conditions are supported by strong negative and some positive evidence, found not only in English Eocene, but in all Tertiary beds throughout the world. In the Lower Bagshot of Hampshire have been found, he states, feather- and fan-palms, *Dryandra*, beech, maple, *Azalea*, laurel, elm, acacia, aroids, cactus, ferns, conifers, *Stenocarpus*, and plants of the pea tribe, together with many others. The question which presents itself to one's mind, he remarks, is, how is it possible that the tropical forms, such as the palms, aroids, cactus, &c., could have grown alongside of the apparently temperate forms, such as the oak, elm, beech, and others? Mr. Gardner's explanation is as follows:—

" Astronomers, having calculated the path of the revolution of the earth in ages past, tell us that in recurring periods each hemisphere, northern and southern, has been successively subject to repeated cyclical changes in temperature. There have been for the area which is now England many alternations of long periods of heat and cold. Whenever the area became warmer, the descendants of semitropical forms would gradually creep further and further north, whilst the descendants of cold-loving plants would retreat from the advancing temperature, *vice versâ*. Whenever the area

became gradually colder, the heat-loving plants would, from one generation to another, retreat further and further south, whilst the cold-loving plants would return to the area from which their ancestors had been driven out. In each case there would be some lingering remnants of the retreating vegetation (though perhaps existing with diminished vigour) growing alongside of the earliest arrivals of the incoming vegetation.

" Such is a possible explanation of our finding these plant-remains commingled together. It must be borne in mind that it is not so much the mean temperature of a whole year which affects the possibility of plants growing in any locality, as the fact of what are the extremes of summer and winter temperature "*.

This is precisely the explanation given by the commingling of subtropical and arctic floras and faunas of deposits belonging to the glacial epoch. The causation in the two cases was in fact the same in principle, differing only in the conditions under which it operated. In the case of the glacial epoch the cold periods were intensely severe and the warm periods but moderately hot; whereas in regard to the Tertiary cold periods they were but moderately cool, and the warm periods exceedingly hot.

Mr. Wallace, who refers to Mr. Gardner's views approvingly, says :—" In the case of marine faunas it is more difficult to judge, but the numerous changes in the fossil remains from bed to bed, only a few feet and sometimes a few inches apart, may be sometimes due to change of climate ; and when it is recognized that such changes have probably occurred at all geological epochs, and their effects are systematically searched for, many peculiarities in the distribution of organisms through the different members of one deposit may be traced to this cause "†.

To prevent having thus to admit the existence of alternate warmer and colder periods during Tertiary times, Mr. Searles V. Wood, Jun., proposed another theory, which, stated in his own words, is the following :—

" The remains upon which the determinations of this flora have been based are drifted, and not those of a bed *in situ* like the coal-seams, and the whole of the Hampshire Eocene is connected with the delta of a great river which persisted throughout the accumulation of the various beds, which aggregate to upwards of 2000 feet in thickness. This river evidently flowed from the west, through a district of which the low ground had a tropical climate ; but like some tropical rivers of the present day, such as the Brahmaputra, the Megna, the Ganges, &c., it was probably fed by tributaries

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* Geological Magazine, 1877, p. 25.
† Island Life, p. 197.

flowing from a mountain-region supporting zones of vegetation of all kinds from the tropical to the Arctic, if during the Eocene period vegetation such as the present Arctic had come into existence, of which we have as yet no evidence. Torrential floods may have swept the remains of vegetation from the temperate zones of this region into tributaries that conveyed it into the main river before it was decayed or water-logged, where it became intermingled with the remains of vegetation which grew in the tropical low ground skirting the main stream, so that both sank together into the same mud and silt "*.

The elevated mountain regions from which he supposes these temperate forms were derived he thinks might have been Mull, 400 miles N.N.W., and Wales 200 miles N.W. Mr. Gardner, however, showed most conclusively that Mr. Wood's theory was based on imperfect acquaintance with the conditions of the problem. The following is Mr. Gardner's reply :—

"The leaves have never been drifted from afar; they are often still adhering to the twigs. The leaves are flat and perfect, rarely even rolled and crumpled, as dry leaves may be, if falling on a muddy surface; still more rarely have they fallen edgeways and been imbedded vertically. They are, moreover, not variously mixed, as they should be if they had been carried for any distance, but are found in local groups of species. For example, all the leaves of *Castanea* have been found in one clay patch, with *Iriartea* and *Gleichenia*; none of these have been found elsewhere. A trilobed leaf is peculiar to Studland; the Alum Bay *Aralia*, the peculiar form of *Proteaceæ*, the great *Ficus*, and other leaves occur at Alum Bay only. Each little patch at Bournemouth is characterized by its own peculiar leaves. Such a distribution can only result from the proximity of the trees from which the leaves have fallen. The forms of most temperate aspect are best preserved, so that to be logically applied, the Drift theory requires the palms, etc., to have been drifted upwards. To suppose that most delicate leaves could have been brought by torrents 400 miles from Mull or 200 miles from Wales, and spread out horizontally in thousands, without crease or crumple, on the coast of Hampshire, may be a feasible theory to Mr. Searles V. Wood, jun., but will not recommend itself to the majority of thinkers " †.

Were there Glacial Epochs during the Tertiary Age?—Many geologists, especially amongst those who are opposed to the theory of recurring glacial epochs, answer this question emphatically in the negative. This belief as to the non-existence of glacial conditions during the Tertiary period is, of course, based wholly on negative evidence; and this negative evidence though strong is by no means perfectly conclusive, and certainly not worthy of the weight which has been placed

* Geological Magazine, 1877, p. 96.
† Ibid. p. 138.

upon it. In Chap. xvii. of 'Climate and Time' I have endeavoured to show that although much has been written on the imperfection of geological records, yet the imperfection of those records in regard to past glacial epochs has not received the attention which it really deserves.

It must be borne in mind, however, that it does not follow from the Physical Theory of Secular changes of Climate, that because the eccentricity may have been high at some particular period there must necessarily have been a glacial epoch. The erroneous nature of this misapprehension of the theory has already been shown at considerable length [*]. Eccentricity can produce glaciation only through means of physical agencies, and for the operation of these agencies a certain geographical condition of things is absolutely necessary. We know with certainty that during the Tertiary period the eccentricity was at times exceptionally high, as, for example, 2,500,000 and 850,000 years ago ; but whether a glacial epoch occurred at these periods depended, of course, upon whether or not the necessary geographical conditions then obtained. Supposing the necessary geographical conditions for glaciation did exist at the two periods in question, still if these conditions differed very much from those which now obtain, the glacial state of things then produced would certainly differ from that of the last glacial epoch. This is obvious, for the same physical agencies acting under very different conditions would not produce the same effects. Under almost any geographical condition of things eccentricity would produce marked effects, but the effects produced might not amount to glaciation. In the Tertiary age, during high eccentricity, the effects resulting might possibly have been as well marked as they were during the glacial epoch; but these effects must have differed very much from those produced at that epoch. We have seen that, owing to that peculiar geographical condition of things existing during the Tertiary period, the physical agents brought into operation by a high state of eccentricity would have a much greater influence in *raising* the temperature of the northern hemisphere when the winters occurred in perihelion, than they would have in *lowering* the temperature of that hemisphere when the winters were in aphelion. At the periods 2,500,000 and 850,000 years ago, for example, those physical agents would no doubt produce quite a tropical condition of climate in high northern latitudes when the winters were in perihelion, while it is quite probable they may not have been able to produce glaciation when the winters were in aphelion. It is more than likely that the

[*] Phil. Mag., February 1884; American Journal of Science, Feb. 1884.

tropical nature of the climate during portions of the Tertiary period was due not so much to that peculiar distribution of land and water existing then, as it was to the fact that this peculiar distribution enabled the physical agents in operation during a high state of eccentricity to impel a vastly greater amount of warm intertropical water into the temperate and Arctic seas than they could have done under the present geographical condition of things.

Those very same geographical conditions enabling the physical agents to raise the temperature exceptionally high during the warm periods would, on the other hand, prevent them from being able to lower the temperature exceptionally low during the alternate cold periods. Nevertheless, I think it probable that at the two periods referred to, when the eccentricity was much greater than it was during the glacial epoch, the temperature would be lowered to an extent that would produce glaciation, although the glaciation might not perhaps approach in severity to any thing like that of the glacial epoch. The negative evidence which has been adduced against the existence of such glacial conditions during the Tertiary period is certainly far from being conclusive.

The opinion is concurred in by Mr. Wallace that the Table of Eccentricity for the past three million years, given in ' Climate and Time,' probably includes the greater part, if not the whole, of the Tertiary period. He states that during the 2,400,000 years preceding the last glacial epoch there were, according to the table, no fewer than sixteen separate epochs when the eccentricity reached or exceeded twice its present amount. But it does not follow, according to the Physical Theory, that there ought, on that account, to have been sixteen epochs of more or less glaciation. Whether such ought to have been the case or not would depend on whether or not the geographical conditions were the same during these epochs as they were at the glacial epoch, a thing regarding which the theory is not responsible. The question is not were there sixteen glacial epochs during the Tertiary period, but were there any? Even granted that those channels assumed by Mr. Wallace did exist, they would not, I feel assured, wholly prevent glaciation taking place at the two periods to which reference has been made, although the glaciation might not be severe.

In support of the opinion that there is no evidence of glaciation during the Tertiary period, Mr. Wallace quotes the views of Mr. Searles V. Wood, Jun., on the subject. Mr. Wood states that the Eocene formation is complete in England, and is exposed in continuous section along the north coast of the Isle of Wight and along the northern coast of Kent from

its base to the Lower Bagshot Sand.   It has, he says, been
intersected by cuttings in all directions and at all horizons,
but has not yielded a trace of any thing indicating a cold and
glacial condition of things.   The same, he adds, holds true of
the strata in France and Belgium.   Further, " the Oligocene
of Northern Germany and Belgium, and the Miocene of those
countries and of France, have also afforded a rich molluscan
fauna, which, like that of the Eocene, has as yet presented no
indication of the intrusion of any thing to interfere with its
uniformly subtropical character."

In reply to all this it may be stated that the simple absence
of any trace of glaciation in the Tertiary deposits of the south
of England certainly cannot be regarded as conclusive
against the existence of an epoch of glaciation during that
period.   Not many years ago geologists denied that there
was any evidence to be found of glaciation in the south of
England, and at the present time there are hundreds of geo-
logists who will not admit that that part was ever overridden
by land-ice.   If it is so difficult to find in that quarter
evidence of the last glacial epoch, severe as that glacial epoch
was, we need not wonder that no trace of glaciation so remote
as that of the Eocene period is now to be seen.   Besides all
this, there is in the south of England the land-surface on
which the glaciation, if any, took place, whereas not a vestige
of the old land-surfaces of the Eocene period now remains.
It therefore seems to me that the mere fact of nothing as yet
having been found in the Tertiary deposits of the south of
England, indicating one or more cold periods, is no proof that
there may not possibly have been such periods, and even of
considerable severity.   The same remarks hold equally true
in regard to the deposits on the continent referred to by
Mr. Wood.

It will be urged in reply that there is one kind of evidence
which ought to be found, as it could not possibly have been
obliterated by the destruction of the Tertiary land-surfaces :
that is, the presence of erratic blocks and foreign rock-frag-
ments imbedded in the strata.   Mr. Wallace states that in the
many thousand feet in thickness of alternate clays, sands,
marls, shales, and limestones no irregular blocks of foreign
material or boulders characteristic of glacial conditions are to
be found.   The same, he says, holds equally true of the
extensive Tertiary deposits of temperate North America.

If it be really the case that the Tertiary beds are wholly
without boulders or fragments of foreign material, then this
certainly may be regarded as proof that no real glacial epoch
could have occurred during that period.   But has it been

satisfactorily ascertained that those beds are wholly devoid of such materials? Those beds, I presume, have been searched by geologists for their fossil contents rather than for strati-graphical evidence of glacial epochs. It is remarkable how long the evidence of glaciation sometimes remains unobserved when no special attention is devoted to the matter. As examples of this, we know with certainty that the Orkney and Shetland Islands were during the glacial epoch over-ridden by land-ice; and yet geologists who had often visited these islands declared that they bore no marks of glaciation. So recently as 1875 the low grounds of Northern Germany were believed to be without glacial striæ; yet when German geologists began to turn their attention specially to the subject, they found not only evidence of glaciation but indisputable proof that during the glacial epoch the great Scandinavian ice-sheet had advanced over the country no fewer than three separate times down to the latitude of Berlin. I have myself seen the striated summit of a mountain on which geologists had been treading for years without observing the ice-markings under their feet. The reason why these markings so long escaped detection is doubtless due to the fact that they were on a spot which no geologist supposed that land-ice could have reached. For this very same reason the fact remained so long unobserved that the low-lying ground of Caithness had been glaciated by land-ice from Scandinavia, filling the entire Baltic and the North Sea. Many similar cases might be adduced where the marks of glaciation remained long unobserved, either because no special search had been made for them, or because they were under conditions in which they were not expected to be found. It is very probable that when the Tertiary deposits are carefully examined, with the special object of ascertaining whether or not they contain evidence of glaciation, geologists may be led to a different conclusion regarding the supposed uniformly warm character of the climate of that period. They may possibly find that, after all, the Tertiary beds do contain boulders and foreign material, indicating the existence of glacial conditions during the period.

Considerable importance has been attached to the statement of Professor Nordenskjöld that he failed to observe in the stratified deposits of Greenland and Spitzbergen any evidence whatever of former glaciation in those regions. "We have never seen," he says, "in Spitzbergen nor in Greenland, in these sections often many miles in length, and including, one may say, all formations from the Silurian to the Tertiary, any boulders even as large as a child's head. There is not the smallest probability that strata of any con-

siderable extent, containing boulders, are to be found in the polar tracts previous to the middle of the Tertiary period. Both an examination of the geognostic condition and an investigation of the fossil flora and fauna of the polar lands, show no signs of a glacial era having existed in those parts before the termination of the Miocene period "[*]. That Prof. Nordenskjöld may not have seen in those strata boulders larger than a child's head may be perfectly true, but that there actually are none is a thing utterly incredible. Still more incredible, however, is the conclusion which he draws from this absence of boulders, viz. that from the Silurian down to the termination of the Miocene period no glacial condition of things existed either in Greenland or in Spitzbergen. Both these places are at present in a state of glaciation; and were it not, as we have seen, for the enormous quantity of heat which is being transferred from the equatorial regions by the Gulf-stream, not only Greenland and Spitzbergen, but the whole of the Arctic regions would be far more under ice than they are. A glacial state of things is the normal condition of polar regions; and if at any time, as during the Tertiary age, the Arctic regions were free from snow and ice, it could only be in consequence of some peculiar distribution of land and water and other exceptional conditions. That this peculiar combination of circumstances should have existed during the whole of that immense lapse of time between the Silurian and the close of the Tertiary period is certainly improbable in the highest degree. In short, that Greenland during the whole of that time should have been free from snow and ice is as improbable, although perhaps not so physically impossible, as that the interior of that continent should at the present day be free from ice and covered with luxuriant vegetation. Perhaps the same skill and indomitable perseverance which proved the one conclusion to be erroneous may yet one day prove the other to be also equally erroneous.

Professor Nordenskjöld does not appear to believe in alternations of climate even in temperate regions, for he says, " from palæontological science no support can be obtained for the assumption of a periodical alternation of warm and cold climates on the surface of the earth."

Evidence of Glaciation during the Tertiary Period. — Evidence of glaciation during the Miocene period is, I think, afforded by the well-known conglomerates and erratics near Turin, first described by M. Gastaldi. Beds of Miocene sandstone and conglomerate, with an intercalated deposit containing large angular blocks of greenstone and limestone,

[*] 'Geological Magazine,' 1875, p. 531.

have been found. Some of these blocks are of immense size. Many of the stones in the deposit are polished and striated in a manner similar to those found in the boulder-clay of this country. It has been shown by Gastaldi that these blocks have all been derived from the outer ridge of the Alps on the Italian side, namely from the range extending from Ivrea to the Lago Maggiore, and, consequently, they must have travelled from twenty to eighty miles. So abundant are these large blocks that extensive quarries have been opened in the hills for the sake of procuring them. The stratification of the beds amongst which the blocks occur sufficiently indicates aqueous action and the former presence of the sea. That glaciers from the southern Alps actually reached to the sea and sent adrift their icebergs over what are now the sunny plains of Northern Italy, is proof that during that cold period the climate must have been very severe. One remarkable circumstance, indicating not only the glacial condition of the bed in which the blocks occur, but also that this glaciation was the result of eccentricity, is the fact that the bed is wholly destitute of organic remains, while they are found abundantly both in the underlying and overlying beds.

Evidence of glaciation during the Eocene period, as is also well known, is found in the "*Flysch*" of Switzerland. On the north side of the Alps, from Switzerland to Vienna, and also near Genoa, there is a sandstone a few thousand feet in thickness, containing enormous blocks of Oolitic limestone and granite. Many of these blocks are upwards of 10 feet in length, and one at Halekeren, near the Lake of Thun, is 105 feet long, 90 feet broad, and 45 feet in thickness. The block is of a granite of a peculiar kind which cannot be matched anywhere in the Alps. Similar blocks are found in beds of the same age in the Apennines and in the Carpathians. The glacial origin of this deposit is further evinced by the fact that it is wholly destitute of organic remains. One circumstance, which indicates that this glaciation was due to eccentricity, is the fact that the strata most nearly associated with the "*Flysch*" are rich in Echinoderms of the *Spatangus* family, which have a decided tropical aspect. This is what we ought, of course, *à priori*, to expect if the glaciation was the result of eccentricity, for the more severe a cold period of a glacial epoch is, the warmer will be the periods which immediately precede and succeed.

Some writers endeavour to account for those glacial phenomena, without any reference to the influence of high eccentricity, by the assumption that the Alps were much more elevated during the Tertiary period than they are at

the present day. If we, however, adopt this explanation, we shall have to assume that the Alps were suddenly elevated at the time when the bed containing the erratics began to be deposited, and that they were as suddenly lowered when the deposition of the bed came to a close—a conclusion certainly very improbable. Had the lowering of the Alps been effected by the slow processes of denudation, it must have taken a long course of ages to have lowered them to the extent of bringing the glacial state to a close. In this case there ought to be a succession of beds indicating the long continuance of cold conditions. Instead of this, however, we have a glacial bed immediately preceded and succeeded by beds indicating an almost tropical condition of climate. When we take this circumstance into consideration, along with the evidence adduced by Mr. J. S. Gardner as to the alternations of warmer and colder conditions in the south of England and other parts of Europe during the Eocene period, the conviction is forced upon us that a high state of eccentricity is the most rational explanation of these curious phenomena.

The greater elevation of the Alps would undoubtedly intensify the glacial condition of things, but it would not originate it. The elevated character of the Alps, for example, was no doubt the reason why the plains of Switzerland, during the last glacial epoch, were so much more buried under ice than other parts of Southern Europe; but their elevation was not that which brought about the glaciation, for those plains were free from ice both before and after the glacial epoch, though the Alps were no doubt as high as they were during the ice-period.

If we adopt the theory that these glacial conditions were due to eccentricity, then we have, as I endeavoured to show many years ago *, a clue to the probable absolute date of the Middle Eocene and the Upper Miocene periods. There were, as we have seen, two epochs during the Tertiary period when the eccentricity was exceptionally high, viz. 2,500,000 years ago and 850,000 years ago. The former might probably be the date of the "*Flysch*" of the Eocene formation, and the latter the date of the period when the Miocene erratics were deposited in the icy sea near Turin.

Some geologists have maintained that the climatic conditions of the Tertiary period are utterly hostile to the Physical Theory of Secular changes of Climate. The very reverse, however, is the case; for, as we have seen, several of the facts of Tertiary climate can be explained on no other principle than that of the theory.

I shall next consider the facts bearing on Arctic Interglacial Periods.

* Phil. Mag., November 1868; 'Climate and Time,' chap. xxi.

XXXIV. *On the Amount of the Atmospheric Absorption.* *By* S. P. Langley[*].

THE earth is surrounded by an absorbing atmosphere, and we never see the sun or the stars except through it.

When we wish to know what the absolute brightness of the sun or of a star is, we must first ask what the degree and kind of this absorption has been, and must add to the directly observed quantities of light the amount that the atmosphere has taken away. Accordingly, every one engaged in such researches must determine in explicit or implicit terms for himself, or take on trust through another, the amount of the absorption, which there is great unanimity in fixing at about 20 per cent. of the whole (at the sea-level). Thus the earliest observations in the last century give the light-absorption as 19 per cent. The very elaborate ones by Seidel of Munich give 21 per cent., those by Pritchard at Oxford 21 per cent.; the most recent, by Mueller, at Potsdam, 17 per cent.; while the observations by Pouillet on the sun's heat give 18 to 24 per cent.; and almost all of a great number which could be cited, whether on light or heat, give about 20 per cent. It has indeed been recognized of late years that the " light "-rays are, on the whole, more absorbable than those of " heat," and that, in particular, blue light is much more so; but the difference between the mean coefficients of " light " and " heat," as found by the usual methods, is so small that we may here continue to speak of this " light "-absorption of 20 per cent. as closely applicable (in common estimation) to heat also. Thus, the very careful series of Ericsson on the sun's heat gives about 21 per cent. In fact, many thousands of observations by scores of observers, during the past and present century, seem to have determined this proportion with all the exactness of which it is capable.

I have arrived at a result so wholly different that, in the face of such authority, I almost hesitate to announce it; for I have been forced to the conclusion that all these determinations are in error, and not in some small degree, but by a quantity probably at least equal to the total amount in question.

I hasten to say, that I do not dispute the general accuracy of the numerous skilful investigators of known repute who have made these determinations, but that I dissent from the method in almost universal use for reducing them; for since it is certain that none of these observers have been outside

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the atmosphere to see what the radiation really is, all of them, however skilful, must depend on inference to determine what it would be, if they could thus observe it. It is certain that nearly all have used a formula of which it seems capable of absolute demonstration that it is not only erroneous, but that its error always lies in one direction, so as to invariably make the calculated absorption too small ; and it may be further shown, with an evidence which seems little less than demonstrative, that the numerical value of the error is very large in relation to the quantities involved.

I have been led, however, not by theoretical considerations alone, but by experimental investigation (during the course of which I have observed both near the sea-level and at great altitudes), to the conclusion that the laws under which solar and stellar light and heat are absorbed by the atmosphere are so complex that their complete comprehension is still beyond our power, but that we may at least now improve our present ways of studying them ; for investigators have, however skilful in their observations, commonly ignored the complexity of the problem of their reduction, and, assuming that it is as simple as we could wish it to be, have proceeded to compute the result by such a formula as would be most convenient for us, if nature would follow. Thus, owing to a natural tendency to accept as sufficient any scientific dogma which has respectable sponsors and which saves labour, the simple rule, established over a century ago by Bouguer, and consecrated by the use of Herschel and Pouillet, to whom it embodied all the knowledge of their time, is commonly used by us to-day ; though we may easily be convinced that it has ceased to express the facts known to us.

To justify this language, let us consider what the problem appears to be at first glance, and what the first suggestion is for solving it. If a beam of sunlight enters through a crevice in a dark room, the light is partly interrupted by the particles of dust or mist in the air, the apartment is visibly illuminated by the light laterally reflected or diffused from them, and the direct beam, having lost something by this process, is not so bright after it has crossed the room as before. In common language, the direct light, to an observer in the path of the beam, has been partly " absorbed," and the problem is, to determine in what degree. If a certain portion of the light (suppose one fifth) was thus scattered, the beam after it crossed the room would be but four fifths as bright as when it entered it ; and, if we were to trace the now diminished beam through a second apartment altogether like the other, it seems at first reasonable to suppose that the same propor-

tion (*i. e.* four fifths of the remainder) would be transmitted there also, and that the light would be the same kind of light as before, and only diminished in amount (in the proportion $\frac{4}{5} \times \frac{4}{5}$). The assumption originally made by Bouguer[*] and followed by Herschel and Pouillet, was, that it was in this manner that the solar heat was absorbed by our atmosphere, and that by assuming such a simple progression the original heat could be calculated. (The minute expenditure of energy in the actual warming of the air is of course to be included.)

Let us (to repeat Bouguer's reasoning) divide in imagination any homogeneous absorbing medium into successive strata of identical thickness and chemical constitution.

Let A be a source of radiant heat or light whose intensity is reduced by passage through the first stratum to (let us suppose) a fraction of the original represented by p, so that what was A becomes Ap. Then, since the second stratum is identical with the first in constitution and amount, and must (it is assumed) have an identical effect, it will, on Bouguer's hypothesis, transmit p of what enters it, and Ap^2 will emerge from the second, and so on, the fraction p transmitted by the unit of thickness (the " coefficient of transmission ") being evidently the common ratio of a geometrical progression, so that if the original heat be A, the amount of heat after passing through e strata will be Ap^e, and the amount transmitted at any point will be proportional to the ordinate of a logarithmic curve.

To apply this to the estimate of the heat outside the atmosphere (*i. e.* before absorption), let SJ be a small portion of
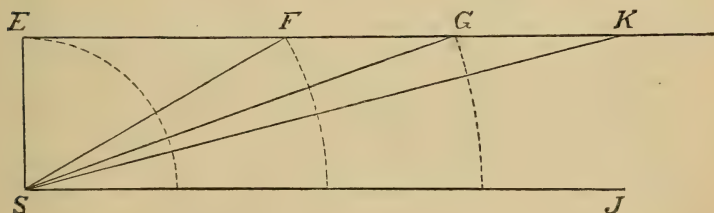
the earth's surface, and EK the upper surface of the atmosphere, which is here supposed to be of uniform density and constitution. (The effects of the actually unequal density of successive strata can, it is assumed, be calculated and allowed for.) Let S be the observer's station, then ES would be the direction of a ray where the sun is in the zenith ; and, to fix our ideas, let FS = 2 ES, GS = 3 ES, KS = 4 ES, &c. The

* Bouguer, ' *Traité de la lumière,*' Paris, 1760.

original heat A would become Ap after passing through one
stratum (ES) ; and, according to what has been assumed, it
would become (when the sun's zenith distance became ESF)
Ap^2 after absorption by the two strata between F and S, Ap^3
after absorption by the three strata between G and S, &c. A,
the original heat, and p, the coefficient of transmission, are
unknown ; but if we make an observation of the heat actually
reaching S along FS (let us call this heat m), and again later
in the day along KS (calling this second observed quantity
n), we have in the particular case supposed

$$A p^2 = m, \qquad\qquad A p^3 = n,$$

whence A and p both become known. Designating the
number of strata by e and the observed value (m or n) by t,
we have then A$p^e = t$; the exponential formula of Pouillet and
later investigators. Its fundamental (and erroneous) assump-
tion is, that the coefficient of transmission (p) is a constant.

It is no doubt true that a very sensible portion of the
solar rays is scattered by an analogous process in our atmo-
sphere ; but we have in our present knowledge to consider
that, by whichever of its effects we note it, this radiation is
not simple, but complex. Thus we must remember that heat,
like light, is of different kinds. To use Melloni's illustration,
radiant light would, to any eye that could *see* it, appear to be
of totally different colours ; and hence, it may be added, we
ought no more to attribute to it a single rate of absorption
with regard to any absorbing medium than to assume that a
blue and a red ray would pass through a red glass with equal
facility. The statement of this fact may perhaps seem
superfluous to the reader, for it has long been in one sense
well known. But in another and most important sense it is
not well known ; and it cannot be superfluous to recall its
bearing on our present research, since it is the neglect to
follow it into its consequences which has led to the error in
question. Since, then, the solar energy, whether regarded
in whole as " heat " or " chemical action," or in part as
" light," is the sum of an infinite number of radiations ; these
may be conceivably influenced in an infinite diversity of ways
by the different atmospheric constituents. In fact the larger
particles rather reflect than diffuse the heat or light, and hence
treat all wave-lengths nearly alike, or diminish the direct
radiation by a nearly general absorption ; minuter ones begin
to act selectively, or, on the whole, more at one end of the
spectrum than the other ; smaller particles, whether of dust
or faintest mist, and smaller still, form a probably con-
tinuous sequence of more and more selective action, down

almost to the actual molecule, whose vibration is felt in the purely selective absorption of some single ray. The effect of the action of the grosser dust-particles, then, is to produce a general and comparatively indifferent "absorption" of all rays, after which the spectrum would everywhere seem equally less bright and less hot. The effect of the molecular absorption is to fill the spectrum with evidences of the selective action in the form of dark telluric lines, taking out some kinds of light and heat, and not others, so that after absorption what remains is not only less in amount, but *altered in kind.* Between these two extreme examples of absorption, we repeat, an unlimited number of others must exist; but we shall need here for simplicity to first treat the whole as coming under one or the other of these two types, a procedure already more accurate than the primitive one followed by Bouguer, Herschel, and Pouillet, but which we recognize as still but a convention, which is imposed on us provisionally by the actual complexity of nature.

It will be seen now more clearly that the whole primitive process followed by Pouillet is an assumption, for it is simply taken for granted that the same proportion will be absorbed by one like stratum as by another. On actually trying the experiment, however, with media in the laboratory, Melloni long since observed that like proportions were *not* absorbed by like strata; and the reason was found in the fact just noted, that radiant energy is not a single emanation, but the sum of an infinity of diverse ones, each with its own separate rate of absorption. It follows that the coefficient of transmission is truly constant only in the case of the absolutely homogeneous ray, which the ordinary photometer or thermometer cannot in the least discriminate, and which the finest linear thermopile or bolometer can but approximately discern; and hence that the original light of the star or heat of the sun, and the amount absorbed, can at best only be found approximately. However familiar this principle may be in some departments of physics, astronomers and meteorologists have been slow in making this application to the present case, but have continued to deduce the brightness of the stars, or the Solar Constant, from observations in which the radiation is either treated as absolutely homogeneous, or in which its non-homogeneity is scarcely recognized as a factor of importance [*].

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[*] Exceptions to this remark are, however, to be made in favour of the very early work of Principal Forbes (Royal Society's 'Philosophical Transactions,' May 1842), and of the more recent labour of M. Crova (*Académie des Sciences de Montpellier*, 1876). See also the excellent

This neglect to make what seems so pertinent an application of Melloni's observation, even after it had been explained and extended (by Biot), will seem more explicable when it is remembered that no direct means of measuring the absorption in even approximately homogeneous rays till very recently existed, and that a departure from the old formula, which ignores the difficulties, involves their recognition, and the devisal of new processes to meet them. Even if we, by the employment of such new processes, succeed in measuring the absorption in approximately homogeneous rays, the approximation is chiefly to homogeneity in wave-length, and not to uniformity of physical properties in consecutive wave-lengths, so that we are unable to represent the absorption as any continuous function of the latter. In other words, we may measure on separate narrow portions ($\Delta\lambda_1$, $\Delta\lambda_2$, &c.) of the spectrum, and determine for each its apparent coefficient of transmission (p_1, p_2, &c.), which is in each case some function of the wave-length; but we are not at liberty to write that the original energy of the heavenly body

$$A = \int_{\lambda_n}^{\lambda_m} (\phi\lambda)^{-\epsilon} d\lambda,$$

since our $\phi\lambda$ is really discontinuous, a remark the import of which will become more apparent in the sequel. For the present at least we are at liberty only to divide the spectrum into a finite number of equal parts, and to mechanically sum them.

I have already stated elsewhere [*] that in neglecting the fact that the absorption is really selective we not only commit an error, but an error that always lies in one way, so that any determination of the absorption we make by the ordinary and erroneous formula never errs by being too great, but is, so far

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little treatise '*Actinométrie*' by M. Radau. The use of two coefficients is proposed in this, as it has been before, but does not seem to have been followed by others, who, like M. Violle, have subsequently (*Annales de Chimie et de Physique*, 1879) employed but a single coefficient of transmission. Still more lately, however, the importance of the consideration on which the writer here insists has been remarked on by Messrs. Lecher and Pernter, and perhaps by others. The employment of the method of Forbes, especially as modified and extended by Crova, appears to be the best means at the command of the observer with the actinometer or photometer. This method, however, is unfortunately very limited in its practical application, owing to the insufficiency of data thus obtainable, and it still gives a necessarily too small result, though a larger one than Pouillet's.

[*] *Comptes Rendus de l'Acad. des Sci.* xcii. p. 701 (March 21, 1881).

as it depends on this formula, always, and invariably, too small. The demonstration may be put in an extremely simple form, but I am not aware that it has been elsewhere given, though it was indicated in the proceedings just cited.

Let us first suppose the radiation of the heavenly body to be really composed before absorption of two portions, A and B. Let A have a special coefficient of transmission (a), and B another, special to itself (b). Then, if we assume (still for considerations of convenience only) that each of these portions is, separately considered, homogeneous, we may write down the results in the form of two geometrical progressions, thus :—

TABLE I.

Original radiation.	Ratio.	Radiation received after absorption by one stratum.	By two strata.	By three strata.	By four strata, &c.
A	a	Aa	Aa^2	Aa^3	Aa^4
B	b	Bb	Bb^2	Bb^3	Bb^4
A+B		$Aa+Bb$ $=(M)$	Aa^2+Bb^2 $=(N)$	Aa^3+Bb^3 $=(O)$	Aa^4+Bb^4 $=(P)$

Then will

$$\frac{Aa+Bb}{A+B} < \frac{Aa^2+Bb^2}{Aa+Bb} < \frac{Aa^3+Bb^3}{Aa^2+Bb^2} \qquad < \frac{Aa^4+Bb^4}{Aa^3+Bb^3} < \&\text{c.}$$

and

$$\frac{Aa^2+Bb^2}{Aa+Bb} < \left(\frac{Aa^3+Bb^3}{Aa+Bb}\right)^{\frac{1}{2}} < \left(\frac{Aa^4+Bb^4}{Aa+Bb}\right)^{\frac{1}{3}} < \&\text{c.} \;\; \ldots$$

The fractions here are the coefficients of transmission, as deduced from observations at different zenith-distances. They evidently differ, and (as will be shown) each is larger than the preceding.

In the above table $Aa+Bb$ is the sum of the two kinds of radiation as observed after absorption by one unit stratum (sec $\zeta=1$) by the photometer or actinometer; Aa^2+Bb^2 is the sum of the radiations observed after absorption by two strata (sec $\zeta=2$) &c.; but we are here supposed to independently know the really dual constitution of the radiation,

which the photometer or actinometer does not discern.   According to the usual hypothesis, the coefficient of transmission, which is the quotient obtained by dividing the value after n absorptions by that after $n-1$ absorptions, or, more generally, that from the expression

$$\left(\frac{\text{Value after } n \text{ absorptions}}{\text{Value after } m \text{ absorptions}}\right)^{\frac{1}{n-m}}$$

is a constant.   It is in fact not a constant, as we shall prove later; but we shall first show that, if we proceed upon the ordinary assumption, the value obtained for the original light of the star before absorption will, in this case, be too small. For, if we observe by a method which discriminates between the two radiations, we shall have, if we separately deduce the original lights from our observation of what remains after one, and, again, after two absorptions, the true sum

$$\text{A} + \text{B} = \frac{(\text{A}a)^2}{\text{A}a^2} + \frac{(\text{B}b)^2}{\text{B}b^2};$$

while if we observe by the ordinary method, which makes no discrimination, we shall have the erroneous equation

$$\text{A} + \text{B} = \frac{(\text{A}a + \text{B}b)^2}{\text{A}a^2 + \text{B}b^2},$$

which is algebraically less than the first, or correct value ; for the expression

$$\frac{(\text{A}a)^2}{\text{A}a^2} + \frac{(\text{B}b)^3}{\text{B}b^4} > \frac{(\text{A}a + \text{B}b)^2}{\text{A}a^2 + \text{B}b^2}$$

readily reduces to the known form

$$a^2 + b^2 > 2ab.$$

Moreover, since $a^2 + b^2 - 2ab = (a-b)^2$, *the error increases with the difference between the coefficients.*

Now, in the general case, if we suppose the original radiation L to be composed, before absorption, of any number of parts A_1, A_2, A_3, $+ \ldots$ having respectively the coefficients of absorption a_1, a_2, a_3, $+ \ldots$, the true value of L is given by a series of fractions which may be written in the form

$$\text{L} = \Sigma \frac{(\text{A}a)^2}{\text{A}a^2} = \Sigma \text{A};$$

whereas the value of the original energy by the customary formula would be

$$\text{L}_1 = \frac{\Sigma(\text{A}a)^2}{\Sigma \text{A}a^2};$$

so that, all the quantities being positive, by a known theorem $L > L_1$; and for the same values of A_1, A_2, A_3, ... this inequality is greater the greater the difference in the values of the coefficients a_1, a_2, a_3, ...

But this is stating in other words that the true values found by observing separate coefficients of transmission are *always* greater than those found when we do not distinguish between the radiations of which the light (or heat) of the star or sun is composed, and also that the amount by which the true values are greater increases with the difference between the coefficients.

We have stated above that the usual hypothesis makes the coefficient of transmission a constant. It will be seen from the above table, however, that it varies from one stratum to the next; that it is least when obtained by observations near the zenith; and that it *increases progressively as we approach the horizon.* For, since a and b are each less than unity, each of the sums $Aa + Bb$ &c. in the above table is less than the preceding. It is also evident that their rate of diminution decreases as we approach the horizon, since

$$Aa^2 - Aa^3 > Aa^4 - Aa^4, \qquad Bb^2 - Bb^3 > Bb^3 - Bb^4.$$

Hence

$$(Aa^2 + Bb^2) - (Aa^3 + Bb^3) > (Aa^3 + Bb^3) - (Aa^4 + Bb^4).$$

Consequently the difference between the numerators of two successive ratios, such as

$$\frac{Aa^3 + Bb^3}{Aa^2 + Bb^2} < \frac{Aa^4 + Bb^4}{Aa^3 + Bb^3}$$

is less than that of their denominators. In other words, although both numerator and denominator decrease in successive ratios, the ratios themselves increase progressively; and a similar demonstration applies to the form

$$\frac{Aa^2 + Bb^2}{Aa + Bb} < \left(\frac{Aa^n + Bb^n}{Aa + Bb} \right)^{\frac{1}{n-1}}.$$

But these ratios are the coefficients of transmission in question.

Further, a simple inspection of the form of the expression

$$Aa^2 - Aa^3 > Aa^3 - Aa^4 \qquad Bb^2 - Bb^3 > Bb^3 - Bb^4$$

shows that what is there demonstrated for two numbers and two coefficients A, a, and B, b, is true for any number, even infinite, which is the case we deal with in actual observation.

In other words, it is universally true that when the numbers are positive, and a, b, c, d, ... proper fractions,

$$\frac{\mathrm{A}a^{n+1} + \mathrm{B}b^{n+1} + \mathrm{C}c^{n+1} + \mathrm{D}d^{n+1} + \ldots}{\mathrm{A}a^n + \mathrm{B}b^n + \mathrm{C}c^n + \mathrm{D}d^n +} < $$

$$< \frac{\mathrm{A}a^{n+2} + \mathrm{B}b^{n+2} + \mathrm{C}c^{n+2} + \mathrm{D}d^{n+2} + \ldots}{\mathrm{A}a^{n+1} + \mathrm{B}b^{n+1} + \mathrm{C}c^{n+1} + \mathrm{D}d^{n+1} + \ldots};$$

and hence universally true, that when the separate coefficients of transmission are positive and less than unity (as is the case in nature), the general coefficient of transmission in the customary exponential formula is—

(1) *Never a constant*, and (as determined from the customary formula),

(2) *always too large*;

(3) *always larger and larger as we approach the horizon*.

(4) The original light or heat of the heavenly body as found by the photometric and actinometric processes, and the formulæ in universal use, *is always too small*, a conclusion which we have just reached by another method.

The above demonstration does not tell us in how great a degree this coefficient is too large, and for aught we have here yet demonstrated the error may be practically negligible.

Since the method ordinarily employed demonstrably gives too small results, the burden of proof might seem to rest on those who still employ it, who might now with propriety be asked to show that the continued use of methods and formulæ certainly in some degree inaccurate does *not* lead to an error at least as great as the total absorption in question. This has never been done. There is a common assumption that if there were any considerable error, its results would become apparent in such numerous observations as have been made all over the world in stellar photometry and solar actinometry during this century, since in these observations of stellar magnitudes, for instance, two stars whose relative magnitudes are positively known give results agreeing with the ordinary formula when one is near the zenith and the other near the horizon. At first this looks almost like evidence that there can be no great error in the determination of absolute magnitudes by the ordinary formula, and yet this apparent proof is demonstrably a fallacy. It is certainly a specious one, but it is absolutely demonstrable that the error *might* be enormous —that the actual absorption might be, for instance, 50 per cent. instead of 20—without this gross discrepancy being detected by our present modes of observation. As the present methods are known to give, as I have just said, values

in substantial agreement (within three or four per cent.) from independent observations made at very different altitudes of the sun or star, the proof of this last statement may well be demanded, and I proceed to give it.

(It is admitted that the original energy is divisible into an unlimited number of rays, each characterized by its own coefficient of transmission, and that these coefficients have values varying from zero to unity.) Let this original energy of the heavenly body be X, and let us denote, as in Table I., the observed energy after one absorption by M, after two by N, after three by O, &c.

The assumption of those who admit the existence of an error but maintain that it is negligible, is that, since we do know that O : N = N : M very nearly, *therefore* N : M = M : X very nearly; or, in other words, that if we can prove that $M = \dfrac{N^2}{O}$ within three or four per cent., we are entitled to assume that there is only a like small error in writing $X = \dfrac{M^2}{N}$.

We can make the fallacy of the preceding assumption most obvious by first considering a particular case. Let the original energy be divided into any number of parts A, B, C, &c., each with its own coefficient a, b, c, &c., so that

$$Aa + Bb + Cc + Dd + \ldots \ldots Kk + Ll \ \&c. = M,$$
$$Aa^2 + Bb^2 + Cc^2 + Dd^2 + \ldots \ldots Kk^2 + Ll^2 \ \&c. = N,$$
$$Aa^3 + Bb^3 + Cc^3 + Dd^3 + \ldots \ldots Kk^3 + Ll^3 \ \&c. = O,$$
$$\&c., \qquad\qquad \&c., \qquad\qquad \&c.$$

We have only to assume that k, l, &c. are sufficiently near zero (so that K, L, and all other rays affected with such coefficients sensibly vanish before they reach the observer) to see that the only quantities sensible to observation are those with relatively large coefficients as A, B, C, D, &c.; so that now

$$Aa + Bb + Cc + Dd + \&c. = M,$$
$$Aa^2 + Bb^2 + Cc^2 + Dd^2 + \&c. = N,$$
$$Aa^3 + Bb^3 + Cc^3 + Dd^3 + \&c. = O.$$

From these values M, N, O, &c. we can never estimate the amount of the extinguished rays K, L, &c., since these do not enter into the observed values by any amount sensible at all.

Now to the rays A, B, C, D, &c., which remain, and to their coefficients, we may evidently assign any values con-

sistent with the conditions, which shall make the difference between $\frac{M}{N}$ and $\frac{N}{O}$ as small as we please, for in the equations

$$\frac{Aa + Bb + Cc + Dd + \&c.}{Aa^2 + Bb^2 + Cc^2 + Dd^2 + \&c.} - \frac{Aa^2 + Bb^2 + Cc^2 + Dd^2 + \&c.}{Aa^3 + Bb^3 + Cc^3 + Dd^3 + \&c.} = R$$

we can always assign positive and real values to A, a, &c., such that R may be as small as we desire.

But R represents here the apparent error of observation, as inferred from a comparison between "high and low stars." Hence it follows that *however close the agreement may be between observations on absorption, made at quite different altitudes of the heavenly body, we have no right to infer that the error of the final result is not indefinitely great.*

If, while the truth of the above proposition is admitted in the abstract, it be still urged that we do not as a matter of fact have reason to suppose that so indefinitely large a part of the solar rays are quite extinguished ere they reach us, I would point out that it is not in reality necessary to suppose the present extreme case (*i. e.* that of a large part of the original radiation being wholly absorbed), which has been taken here only to make the nature of the argument more evident.

For if we agree (as we certainly may) that a notable portion of the coefficients are near zero, and another notable portion still but small fractions of unity, what we have just shown for an extreme case will also follow for the usual one, for it follows from the previous demonstration that the greater the discrepancy between the coefficients the more shall we underrate the true absorption, and the greater will be our error. To see what the conditions actually are, in inferring it from the ordinary formula, we must now consider more narrowly how this telluric absorption takes place. I have already spoken of the general or non-selective absorption, whose extreme type is the scattering of light by large dust-particles in a sunbeam, and now proceed to consider the other typical extreme, which is that of purely selective absorption.

I have here some photographs*, which I owe to the kindness of Professor Rowland of Baltimore, in which we have a portion of the spectrum near D, photographed when the sun was on the meridian, and a second photograph of the same limited portion, at about half-past three in the afternoon, when the air-mass traversed was only about one half greater. Notice nevertheless the immense difference caused by the

* Not given here.

growth of telluric lines in this short interval. There is scarcely a hair's breadth of the plate which they have not invaded. It is true the whole spectrum is not so densely crowded with them as this region is, and yet, broadly speaking, we may say that almost the entire spectrum is visibly filled with telluric lines, in all but juxtaposition, just before sunset.

What is a telluric line? A very narrow black and cold region where the absorption has already done its full work, or which is, at any rate, so black and so cold that it can grow very little blacker or colder. The extinction of the ray here is nearly absolute, or, in other words, its coefficient of transmission is very small indeed. If we consider the same part of the spectrum at noon, we find that the region occupied by these lines must in reality be darker than if there were no absorbing air, even if the absorption has not progressed so far that the individual absorption-lines are visible, or distinctly black. But, in fact, we do see parts of them distinctly black, even at noon. Moreover, if we climb a mountain into the upper air, we find great numbers of these rays practically extinguished even there, long before they have reached the observer at sea-level. In this way I have myself observed numerous telluric lines quite black on Etna*, and even at greater altitudes, in the pure dry air of the Sierra Nevadas of California; so that there is every reason to believe that at the highest altitudes attainable by man certain portions have already disappeared from the spectrum, and that we cannot correctly infer the original condition by any amount of observation on the different rates of absorption of what remains. Irradiation makes the telluric line appear narrower and weaker than it really is. Photography, in this respect, is a much more trustworthy guide; and I think that those of us who are used to seeing the spectrum of a low sun, and who have gathered any impression of thinness and rarity of these lines, may correct our ideas with advantage by the study of these admirable photographs, of which I will only observe that when they were taken the air-mass at noon was 1·09 and in the afternoon 1·60; so that all this increase of telluric lines came with a very little increment of the absorbing air, and is but a small part of what we should see nearer sunset. Evidently the noon spectrum must be less bright, not only for the telluric lines distinctly seen but for those indistinctly seen individually, or latent only, and which come out as separate individual lines when the sun is lower. It results from what has just been said, then, that the part of the absorption due to telluric lines alone is more considerable than is commonly

* See also the important observations by Professor Smyth on Teneriffe.

thought, and that the coefficients of absorption and transmission, which have been obtained by various writers on actinometry and photometry, are really in general the mean coefficients obtained from the average of hundreds of these alternations (and necessarily too small); and yet, more than this, that the smallest part included in the field of the experiment, whether the telluric lines are separately visible or whether they are only latent there, is filled with alternations of transmission and absorption, and therefore, according to our previous demonstration, the mean result, even when obtained by a linear thermopile or bolometer, must still indicate too feeble an absorption. I speak now only of the strictly selective absorption; but I again remind the reader that there is also the partly selective and comparatively non-selective absorption already mentioned, and that practically between the telluric line and the general absorption we have every intermediate coefficient of transmission from unity to zero. The previous criticism applies then, though in a less degree, to the few investigations where two or three coefficients have been used, and even to investigations with the linear thermopile or bolometer, using numerous coefficients, among which I mean to include my own. I have done all I could to minimise the error by measuring on rays as nearly homogeneous as possible —that is, by measuring on parts of the spectrum so narrow that they may be called, without exaggeration, linear, a name which we may certainly apply to a hair-like line $\frac{1}{5}$ of a millim. in width, forming the working face of the linear bolometer; but even this strip, when laid down in the spectrum, covers more than the distance between the D lines; and if we fix our attention on that well-known region as a type, we see that this hair-like line itself covers in this narrow interval alone at least a dozen alternations between brightness and almost total extinction, so that though in respect to wave-lengths we may be said to measure approximately homogeneous rays with a linear instrument, in respect to this local absorption we do not. I am convinced that no one knows what this absorption really is in amount; but I think we can now begin to see somewhat of what it is in kind, and we may be prepared to agree that the data in the annexed table (Table II.) may represent numerically the proportions of nature with a certain approximation. In this table (II.) we have certain numerical results consequent on the approximative hypothesis that the total heat in sun or star is divided into a certain finite number of parts, each one of which has its own rate of absorption.

Here the radiant energy before absorption is supposed to

be divided into ten parts, A, B, C, ... J, each having its separate coefficient of transmission a, b, &c.—an arrangement which may be taken to represent some sort of adumbration of the complexity of nature's problem and the method of her work. It is given here only in illustration of the kind and degree of the errors induced by use of the usual formulas ; and the demonstration already given in no way depends on these numerical values, whose approximate exactness I do not need to maintain, since they are offered merely as a numerical illustration and in justification of the previous assertion, that the absorption at any rate *may* be more than double what we think it (as in this specific case) without our having means of knowing of our error through our present formula.

It may, however, be incidentally observed that these values do typify the facts, with a certain approximation to the real values of nature, for they are obtained by approximate solution of equations of the form

$$Aa + Bb + Cc + Dd + Ee \text{ &c.} = M,$$
$$Aa^2 + Bb^2 + Cc^2 + Dd^2 + Ee^2 \text{ &c.} = N,$$
$$Aa^3 + Bb^3 + Cc^3 + Dd^3 + Ee^3 \text{ &c.} = O,$$

where M, N, O, &c. do not differ widely from the results of observation. The conclusion in this specific case therefore seems fairly typical of that in the general one.

We have here supposed that the radiant energy from the sun or star before it enters our atmosphere is divided into ten equal parts, each of which in general suffers some different partial absorption. While no ray may be absolutely absorbed or wholly transmitted, a certain small part (represented in the spectrum by known telluric lines) is so nearly absorbed, that its coefficient in the first decimal place would be 0, and a certain more considerable portion, corresponding in a general sense to certain infra-red rays, has coefficients here undistinguishable from unity. Probably the greater part of the spectral energy, however, is intermediate between these two extreme types, and so our numerical values indicate.

The first column is the original intensity before absorption (we have in this particular example, for simplicity, supposed A = B = C . . . . = J = 1, though this condition is not necessary. It will be observed, however, that under it in the second column $Aa = a$, $Bb = b$, &c., so that the coefficients of transmission, the ratios of each geometric progression, are the same in this particular column as the intensity after absorption).

TABLE II.

I.	II.	III.	IV.	V.
Original intensity (ordinarily unknown).	Observed intensity after one absorption.	Observed intensity after two absorptions.	Observed intensity after three absorptions.	Observed intensity after four absorptions.
A, B, C, &c.	Aa, Bb, Cc, &c.	Aa^2, Bb^2, Cc^2, &c.	Aa^3, Bb^3, Cc^3, &c.	Aa^4, Bb^4, Cc^4, &c.
1	·01	·0001	·000	·000
1	·1	·01	·001	·0001
1	·2	·04	·008	·0016
1	·6	·36	·216	·1296
1	·7	·49	·343	·2301
1	·7	·49	·343	·2301
1	·8	·64	·512	·4096
1	·9	·81	·729	·6561
1	·9	·81	·729	·6561
1	1·0	1·00	1·000	1·0000
$10=$ $A+B+$&c. $=X$	$5·9=$ $Aa+Bb+$&c. $=M$	$4·65=$ Aa^2+Bb^2+&c. $=N$	$3·881=$ Aa^3+Bb^3+&c. $=O$	$3·3143=$ Aa^4+Bb^4+&c. $=P$

If we determine the coefficients of transmission from a comparison of II. and III., we have $\dfrac{N}{M}=·789$; if from II. and IV., we have $\left(\dfrac{O}{N}\right)^{\frac{1}{2}}=·812$; if from II. and V., we have $\left(\dfrac{P}{O}\right)^{\frac{1}{3}}=·825$; and the corresponding mean absorptions are

$$1-\frac{N}{M}=0·21,\quad 1-\left(\frac{O}{N}\right)^{\frac{1}{2}}=0·188,\quad 1-\left(\frac{P}{O}\right)^{\frac{1}{3}}=0·175.$$

So that all our observations at different altitudes are in substantial agreement in indicating an absorption of from 18 to 21 per cent., while yet all our inferences from them are quite wrong.

If we observed by some method which discriminated between the different radiations of which the heat or light is composed, we should have, from the observations in columns II. and III.,

$$A+B+C+\ldots J=\frac{(Aa)^2}{Aa^2}+\frac{(Bb)^2}{Bb^2}+\frac{(Cc)^2}{Cc^2}+\frac{\ldots(Jj)^2}{Jj^2}=$$

$$\frac{·01}{·0001}+\frac{·1}{·01}+\frac{·2}{·04}+\&c.\ldots=10$$

(the true value); while the ordinary and erroneous method, which does not discriminate, gives

$$A + B + C + \ldots = \frac{(Aa + Bb + Cc + \ldots)^2}{Aa^2 + Bb^2 + Cc^2 + \ldots} = \frac{(5.9)^2}{4.65} = 7.5 \text{ nearly.}$$

We give the most favourable case for the observer, where (what is rarely or never actually possible) he begins his observations with the sun or star in the zenith, in a sky so changelessly serene that he may continue them up to a point where secant $\zeta = 4$ (corresponding to column V.), and where the altitude is less than 15°. And we here suppose ourselves to have a prior knowledge both of the actual amount of the light or heat before absorption and of its composition, while he is assumed to attempt to deduce the prior amount by the usual formula, and from the usual observations made in the gross by the photometer or actinometer.

The successive values of the absorption thus found by comparing a zenith observation with three successively lower altitudes are 21 per cent., 19 per cent., 18 per cent. All agree much within the probable error of actual observation, as observers conversant with this matter will readily admit, and yet the actual value is all the while

$$1 - \frac{5.9}{10.0}, \text{ or 41 per cent.}$$

It will have been noticed, in fact, that the determinations of this absorption-coefficient by various observers already cited differ among themselves as much as these values do from each other; and if these conditions represent those of nature, the result must be, in practice, that years of observation will be accordant in giving the wholly wrong absorption of from 19 to $22\frac{1}{2}$ per cent., and that the actual minute systematic discrepancies pointed out by our theory, and which are significant of some error in the formula, would probably remain long undetected. While the observer, then, we admit, has strong apparent evidence from the close agreement of his observations that, if there be an error in his formula, it is practically negligible, yet this evidence, according to our demonstration, is fallacious, and the actual error, as appears from the numerical illustration, *may well exceed double the amount* in question, for the above values might evidently be increased without imposing any conditions but such as it may be reasonably assumed are those of nature.

The writer believes the actual mean absorption of sun- and star-light to be at its minimum not improbably over 40 per cent. at the sea-level; but were the stars alone in question, the fact would have but little importance, since their relative magnitudes (unless considerable colour is present) remain

nearly the same with the false hypothesis as with the true one, and it is with their relative magnitudes that the student of stellar photometry is chiefly concerned, for he desires to know their relative brightness at the zenith rather than their absolute brightness outside the atmosphere.

With the sun, however, it is otherwise, for here it is the absolute heat or light which is in question.

Accordingly, when we apply our above conclusions to problems either of solar physics or of meteorology, the result is of an altogether different importance. Almost all the phenomena of meteorology would become predictable if we knew how much heat reaches the soil, and how much, and in what altered kind, is returned to outer space. To solve these problems we must know how much is absorbed by our atmosphere; and there are further reasons, independent of those cited, for believing that this is more than double what is commonly supposed.

It may be observed that the comparison of observations at the base and summit of a very high mountain will enable us to obtain much better determinations than the method of high-and low-sun observations, not only on account of the diminution of the absorbing air-mass, but because we thus avoid certain systematic differences between the atmospheric conditions at noon and evening (or morning) which introduce constant errors into the results, in addition to those already considered. From such observations I have been led, independently of theory, to conclude that the absorption is greater than is commonly supposed. But beside this method, which is in reach of but few, there is another at the command of all, the significance of whose results seems to have been hitherto overlooked.

If we are willing to agree that solar heat is not absorbed by our air in the sense of being accumulated there (since this would heat the atmosphere to the condition of a glowing gas), we must, it seems to me, admit that it is mainly diffused toward and away from us by particles, so that nearly all we lose by selective absorption from the direct light and heat of the sun we ought to find reflected or selectively diffused to us from the sky, or turned away from us to outer space *. I have been engaged in measuring the heat and light from the sky around the sun, and that from the whole sky apart from the sun. These measures are still incomplete, and I will only

* See the investigation of Tyndall on the cause of the blue colour of the sky (Proc. Roy. Soc. vol. xvii. p. 223). See also the theoretical investigations of Clausius (Poggendorff's *Annalen*, vol. cxxix. p. 330 *et seq.*), and of Lord Rayleigh (Phil. Mag. Feb. 1871 *et seq.*).

say that they seem to show that the average amount of blue light (to speak for the moment of blue light only) which is thus scattered from an ordinary pure and cloudless sky at the sea-level already represents a selective absorption of much over 40 per cent. of the original blue in the direct sunlight; but that also the *mean* diffusion is, though less than this, still over 40 per cent., and hence that to obtain the actual light of sun or star before absorption we must add, at any rate, over 40 per cent. to the observed value. To make the meaning of this last statement clear, it may be observed that if there were bright clouds in the sky we should have (as we know by experience) more light from the clouds than from an equal portion of the blue, but that in this case our observing station would gain the added light at the expense of those portions of the earth which were in the clouds' shadow; and in this case, therefore, we should not be justified in adding the light we receive to the observed sunlight to obtain that before absorption. But with a uniform sky it follows that every point on the horizon enjoys the same sunshine that we do at our own station; and hence it is evident that if the atmosphere were taken entirely away the sun would grow brighter by all the light which the atmosphere now sends us, and, in fact, by much more, since this atmosphere is scattering light not only towards us, but also to outer space.

Roughly speaking, we may say that we receive on the average at the sea-level as much light from the sky as we do from the sun itself—getting more light from the sun at midday than from the sky, but more in the morning and afternoon from the sky than from the sun. There is no reason to believe that any smaller proportion of starlight is diffused earthward, and this is independent of that which is diffused toward outer space.

All my own investigations, whether through observations at the sea-level or at an altitude of nearly 15,000 feet, lead me to believe that at any rate the mean absorption of light (and of heat also) by our atmosphere is probably *at least double* that which is customarily estimated; and also to conclude that fine dust-particles, both near the surface and at a great altitude, play a more important part in this absorption, both general and selective, than has been heretofore supposed. I hope soon to make public the result of an investigation into the composite character of the radiation as an indication of what the sky has selectively borrowed from the direct solar rays.

XXXV. *On the Electromagnetic Rotation of the Plane of Pola-*
rization of Light by means of Iron, Cobalt, and Nickel. By
A. Kundt[*].

D R. KERR has shown[†] that the plane of polarization of
the light reflected normally from the polished pole of
an electromagnet suffers a rotation. The direction of the
rotation is opposed to that of the magnetizing current, and
consequently to that of the amperian molecular currents of
the magnet. Kerr has further examined the reflection of
light at the polished side-face of a magnet. He found that
here also a rotation of the plane of polarization takes place
when the electromagnet is excited or has its magnetism
reversed. The phenomena are, however, somewhat complicated.

Plane-polarized light which is reflected at any angle from
a metallic surface retains its plane of polarization only in the
cases in which that of the incident light is coincident with
the plane of incidence, or at right angles to it. In all other
positions of the plane of polarization the reflected light is
elliptically polarized ; Kerr therefore confined his investiga-
tions to the first two cases. He finds that if the polarizing
and analyzing nicols are at right angles, then when the
magnet is excited the field of view becomes bright, which he
interprets as a rotation of the plane of polarization produced
by the magnetization. The direction and the amount of
this rotation are not dependent simply upon the angle of
incidence, but are different also according as the plane of
polarization of the incident light (the long diagonal of the
section of the nicol) is coincident with, or at right angles to,
the plane of incidence.

If the light is polarized in the plane of incidence, the direc-
tion of rotation is the same for all angles of incidence, and
opposed to that of the amperian molecular currents of the
reflecting magnet.

If the plane of polarization is at right angles to the plane
of incidence, then for angles of incidence from 0° to about 80°
the direction of rotation is the same as that of the amperian
currents, but opposed to it for incidences between 80° and 90°.
The amount of rotation is in both cases a maximum for an
angle of incidence of about 65°.

There is also a rotation with oblique incidence of the light
upon the polished pole-surface of an electromagnet. The
direction of the rotation according to Kerr, so far as I can
gather from his data, is the same for all angles of incidence

and opposed to the molecular currents, whether the plane of polarization of the incident light is coincident with, or at right angles to, the plane of incidence.

In all the experiments of Dr. Kerr the magnitude of the rotation is very small—in favourable cases it amounts only to a few minutes; and Kerr has consequently made no measurements, but has only estimated the amount of rotation in the different positions and determined its direction. Some two years ago I repeated Kerr's experiments. My experiments completely confirmed all Dr. Kerr's statements; with the one exception that, upon reflection at the surface of a pole, I obtained also a reversal in the direction of rotation at an incidence of about 80°, when the plane of polarization of the incident light and the plane of incidence were at right angles to each other. This reversal seems to have escaped Dr. Kerr. I have thus succeeded in bringing all the phenomena of reflection at the side faces as well as at the poles of the magnets under one point of view, from which possibly an explanation of the same may result.

That a rotation of the plane of polarization takes place at perpendicular incidence upon the pole-surface of an electromagnet has been further confirmed by Gordon*. He obtained a rotation of 26′ 45″ upon reversal of the magnetizing current.

Then Hall† has shown that with cobalt and nickel also, when they form the pole of a magnet, a rotation of the plane of polarization in the direction opposite to that of the magnetizing current takes place. It may be further mentioned that Hall has also examined whether the plane of polarization of the light which traverses a very thin transparent film of nickel is rotated. The transparent film was prepared according to the method given by Wright, by deflagration of a nickel electrode in a Geissler tube. Hall examined two nickel mirrors, but was not able to perceive any rotation, and remarks that "both these experiments on direct transmission have been, we may say, quite negative."

Lastly, we must mention also that Fitzgerald has endeavoured to give a theoretical explanation of the rotation produced by magnets. I shall further on briefly state Fitzgerald's theory, and show that it is not in agreement with the observations.

I have now recently measured the electromagnetic rotation of the plane of polarization upon reflection from iron, cobalt, and nickel, and completely confirmed my previous experiments

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* Physical Treatise on Electricity and Magnetism, ii. p. 261.
† Phil. Mag. 1881, 5th series, xii. p. 171.

and also those of Kerr. I shall further on briefly review the quantitative results obtained.

I have, however, succeeded in rendering Kerr's experiments decidedly more complete by another method; since, having prepared thin transparent films of iron, cobalt, and nickel, I have examined the rotation of the plane of polarization produced upon passage of light through these films. The result is as follows:—

Transparent films of iron, cobalt, and nickel in the magnetic field rotate the plane of polarization of transmitted light very powerfully. The rotation produced by iron for the mean rays of the spectrum is more than 30,000 *times as great as that produced by glass of equal thickness. The rotation takes place with all three substances in the direction of the magnetizing current.*

After a few brief remarks upon the mirrors and transparent films employed, I give in what follows, first of all, observations upon the electromagnetic rotation upon transmission through metals; then my experiments upon the rotation which is produced by reflection of light from metals; then are included, and added at suitable points, general discussions of the experiments and the conclusions drawn from them.

I. *The Mirrors and Transparent Metallic Films employed.*

In the experiments upon reflection, I at first employed circular steel mirrors of 35 millim. diameter and 6 millim. thickness, of a very high polish. The mirrors were either placed between the poles and suitably fastened there, or attached laterally to the clamps uniting the poles. Any possible distortions were examined by observing in a telescope the images of horizontal and vertical millimetre-scales reflected in the mirrors. Any distortions or changes in the position of the mirrors would be recognized by small irregularities and displacements in the images given by the mirrors. In the series of experiments with mirrors, such as described later on, no irregularities were detected by means of the scale and telescope by which the optical effects observed could have been explained. Then I have employed mirrors consisting of speculum-metal, which had been electroplated with iron or nickel. And, finally, I employed plate-glass mirrors, coated electrolytically with very thin transparent films of iron.

If a glass surface is to be electroplated with a metal, the glass surface must first of all be made conducting. I tried to silver glass in the usual way and then to deposit the iron upon this layer of silver; but so far these attempts have not led to any result. So soon as the current was closed, and iron or

other metal began to deposit itself from the solution upon the silver, the film came off the glass in shreds. With a very good film of silver and exactly adjusted strength of current it might be possible to coat the silver with another metal electrolytically; at least I have at times succeeded in coating small pieces of silvered glass with copper; but I have not pursued the attempt further, since a more convenient method presented itself. M. König, in Paris, for the rotating mirrors employed in his acoustical apparatus uses plate-glass, into one surface of which a very thin transparent reflecting film of platinum has been burnt. The film of platinum is so thin that it is very transparent. Whether it is absolutely continuous is not of any consequence; at least it conducts so well that it may be made an electrode, and covered with a reflecting layer of another metal of any desired thinness.

I have deposited iron according to Varrentrapp's method [*]; cobalt and nickel from solution of the ammonio-sulphates of cobalt or nickel. The concentration of the solution and strength of current must be adjusted according to the thickness which the film is desired to have. I have further coated some of the iron and nickel films with reflecting surfaces of gold, silver, or copper. These metallic films may easily be obtained so thin that they, together with the platinum, are quite transparent.

The incident white light becomes brown when it traverses the iron film, grey with nickel, and bluish grey with cobalt. The surfaces of the deposited films usually reflect very well; but the physical peculiarities of the different surfaces seem to be somewhat variable. Possibly the metals are in certain cases deposited in a crystalline condition. If we cut a long strip from an iron film, it may easily be converted into a permanent magnet by rubbing with another magnet. It is known that the coercive force of galvanically deposited iron is very large.

We are thus able to prepare permanent *transparent* iron magnets, as also transparent magnets of cobalt or nickel.

When suspended by a silk fibre, these transparent magnets adjust themselves perfectly well in the magnetic meridian under the influence of the earth's magnetism.

I hope to study the behaviour of these very thin transparent magnets later on.

II. *Rotation of the Plane of Polarization of Light by its Passage through Iron, Cobalt, and Nickel.*

A Ruhmkorff's electromagnet of the usual construction was

[*] Muspratt's *Chemie,* vol. ii. p. 1200.

employed for these experiments. The iron core, wrapped with wire, was provided with conical, rounded, and perforated pole-pieces. The poles were placed about 4 millim. apart. The current, which was furnished by a Gramme machine, had an intensity of about 16 amperes. The glass plate under examination with its metallic covering was placed midway between the poles in a suitable holder, permitting both horizontal and vertical displacement and rotation, as nearly as possible at right angles to the direction of the rays of light which traversed it. Sunlight was always employed.

In order to measure the rotation produced by the film of iron, cobalt, or nickel, a portion of the piece of glass not covered with the electrolytic deposit of metal was compared with a portion covered by the film, by determining first the rotation produced by glass and platinum, and then determining the rotation due to glass, platinum and iron, cobalt, or nickel. Usually the thin platinum layer produced no measurable rotation; so that a portion of the glass covered by the metallic deposit could be compared with a portion from which the metal and platinum had been removed by means of acid. Since the rotation produced by platinum and glass alone, or by the platinum and glass together with the coating of iron, cobalt, or nickel gave rise to a tolerably strong dispersion, the adjustment was made in these experiments for the transition-tint between blue and red; so that the rotation was determined for the mean rays of the spectrum. When not otherwise specified, the rotation given in the following account means the sum of the rotations in both directions produced by reversal of the current. A rotation in the direction of the amperian currents is further specified as positive, and that in the opposite direction as negative.

Iron.

Iron mirror No. 1.   Brown, transparent.

	°	′
Rotation due to glass and platinum upon reversal of current	+1	0
Rotation due to glass, platinum, and iron	+4	30
Rotation produced by iron film	+3	30

Iron mirror No. 2.   Very thin, light brown, transparent.

Glass and platinum	+1	30
Glass, platinum, and iron	+2	24
Rotation due to iron	+0	54

Iron mirror No. 3.

Glass and platinum	$+1°\ 42'$
Glass, platinum and iron	$+3\ 48$
Rotation due to iron	$+2\ 6$

Iron mirror No. 4:—

After this mirror had been covered with a tolerably transparent layer of iron, half of it was covered with a further deposit of iron; so that this half was dark brown, though transparent. The platinum and iron were then removed from one portion of the glass.

Rotation by glass alone.	$+2°\ 12'$
„ glass, platinum, and thin iron film	$+3\ 42$
„ glass, platinum, and thick iron film	$+5\ 54$
Rotation produced by thin iron film . .	$+1\ 30$
„ „ thick „ . .	$+3\ 42$

As already remarked, the rotation produced by the film of platinum is not measurable.

Cobalt.

Cobalt mirror No. 1.

Rotation by glass and platinum	$+1°\ 18'$
„ glass, platinum, and cobalt .	$+2\ 36$
Rotation by cobalt	$+1\ 18$

Cobalt mirror No. 2. Very transparent.

Rotation by glass and platinum	$+1\ 30$
„ glass, platinum, and cobalt .	$+2\ 34$
Rotation by cobalt	$+1\ 4$

Cobalt mirror No. 3. A portion of the same piece as No. 2.

Rotation by glass and platinum	$+1°\ 30'$
„ glass, platinum, and cobalt .	$+2\ 30$
Rotation by cobalt	$+1\ 0$

The two mirrors placed one behind the other still transmitted sufficient light. The rotation produced by the two cobalt layers together was found to be the sum of those produced by the two separately, viz.:—

Rotation due to 2 and 3 together . . .	$+2°\ 5'$

Cobalt mirror No. 4.

Rotation due to glass and platinum	.	.	$+\overset{\circ}{1}$	$\overset{\prime}{3}$
„	„	glass, platinum, and cobalt	$+3$	1
Rotation due to cobalt .	.	.	.	.	.	.	$+1$	58

Nickel.

I give observations with two good homogeneous mirrors :—

No. 1.

				$\overset{\circ}{}$	$\overset{\prime}{}$
Rotation due to glass and platinum	.	.	$+1$	26
„	„	glass, platinum, and nickel	$+2$	5
Rotation due to nickel .	.	.	.	.	$+0$	39

No. 2.

Rotation due to glass and platinum	.	.	$+1$	35
„	„	glass, platinum, and nickel	$+2$	24
Rotation due to nickel .	.	.	.	.	$+0$	49

The question may now arise whether the rotations obtained for iron, cobalt, and nickel are actually produced by these substances, or whether the observations admit of being explained in any other way. Since in these experiments portions of glass coated with magnetic metal and coated only with platinum are successively brought between the conical magnetic poles, it might be thought that the intensity of the magnetic field between the poles might be different in the two cases, and that the difference in rotation might be thus brought about. I have convinced myself by numerous and varied experiments that even when large masses of iron are brought into the field, neither the rotation of the iron mirror nor that of a piece of glass is perceptibly altered.

It might further be supposed that the thin, strongly magnetic film of iron which clings close to the glass might have some special unknown influence upon the power of rotation possessed by the glass, and the difference observed in rotation between the glass covered with iron and without this covering should be attributed to this effect. In order to decide this point, I placed between the poles a narrow vessel with plane glass sides filled with carbon sulphide, and placed in this a portion of the platinized glass not coated with iron, and determined the rotation produced by the whole system; then a portion of the platinized glass coated with iron was put in the fluid, and the rotation again determined.

In the first case there was a rotation of $+11°\ 25'$

,,   second   ,,   ,, $+12\ 27$

<div align="center">Difference . . . . $+\ 1\ \ 2$</div>

If the platinized glass was placed between the poles without using the sulphide of carbon—

The rotation obtained was . . . . . $+1°\ 11'$

And for the glass with iron . . . . . $+2\ 13$

<div align="center">Difference . . . . . $+1\ \ 2$</div>

Exactly the same as before.

We see that the rotation of the sulphide of carbon which is in as close contact with the iron as the glass is, is not at all influenced by it. We cannot therefore avoid the conclusion that the difference $1°\ 2'$ in both cases is the rotation produced by the iron.

III. *Dispersion produced by Rotation, Specific Rotatory Power, and Circular Double Refraction of Iron, Cobalt, and Nickel.*

Since lately there has frequently not been sufficient sun for the purpose, I have not been able to make extended experiments on the rotation of the plane of polarization for the different colours produced by iron, cobalt, and nickel. Nevertheless I have been able to recognize with certainty that iron has an anomalous rotatory dispersion. Light which had passed through a tolerably dark red glass was rotated perceptibly more powerfully than blue light obtained by passing the sun's rays through ammoniacal copper-sulphate solution.

Corresponding experiments with cobalt and nickel gave only a feeble rotatory dispersion. Experiments in which the red and blue rays of a somewhat impure spectrum were employed showed also an anomalous rotatory dispersion in the iron.

The specific rotatory power of iron was determined with as good a mirror as possible.

The thickness of the iron film obtained by weighing the mirror before and after coating it with iron with the battery was found to be $0 \cdot 000055$ millim.; the rotation for the mean rays of the spectrum produced by glass and platinum was $1°\ 37'$, and that produced by glass, platinum and iron $3°\ 25'$: consequently that produced by iron $1°\ 48'$; the thickness of the platinized glass was $1 \cdot 61$ millim. Consequently the iron rotates some 32,000 times more than the glass used.

With another mirror, whose thickness was 0·000069 millim., the rotation of the iron was found to be 35,000 times as great as that of the glass.

Cobalt has a specific rotation nearly the same as that of iron. Nickel, on the other hand, is decidedly weaker. Two nickel mirrors gave a mean rotation of 14,000 times that of the glass.

I, of course, regard these numbers as approximate only, since the determination of thickness by weighing is very inexact. They give occasion, however, for some interesting conclusions.

According to the experiments of Righi[*], a circularly-polarized ray in which the motion of the æther-molecules takes place in the same direction as that of the molecular currents, traversing a substance which, in a magnetic field, produces rotation in the same direction as the amperian currents, advances more rapidly than a circularly-polarized ray in which the æther-molecules move in the opposite direction. There is therefore a circular double refraction. If n and n' are the indices of refraction for the two opposite circular rays, and ϕ the amount of the observed rotation, d the thickness of the substance traversed by the ray, and λ the wave-length; then

$$\phi = \frac{\pi \cdot d}{\lambda}(n + n').$$

If we take $\lambda = 0\cdot00058$, for d the thickness of iron film given above, viz. $0\cdot000055$, $\phi = 1° \ 48'$, we have

$$(n - n') = 0\cdot1.$$

This difference in refractive index amounts to more than half of that between the ordinary and extraordinary rays in Iceland spar, and is about ten times as great as the difference of refractive indices in quartz at right angles to the axis.

The difference of the refractive indices for the two circularly-polarized rays in the direction of the axis in quartz, according to Lang, amounts only to $0\cdot0000718$.

The film of iron used has therefore, in the magnetic field which I have employed, a rotation 1462 times as great as the natural rotation in quartz of the same thickness as the iron film. It will be necessary to return later on to the circular double refraction of our iron films when we come to speak of Fitzgerald's theory.

* *Nuovo Cimento,* iii. p. 212 (1878).

IV. *Rotation of the Plane of Polarization upon Normal Reflection from Iron, Cobalt, and Nickel.*

For these experiments also Ruhmkorff's electromagnet was employed. The perforated pole furthest from the observer was replaced by a solid pole without perforation. By reflection at a glass plate inclined at an angle of 45° to the axis of the pole, light was sent through the perforated limb of the electromagnet, reflected at the metal plate placed between the poles, and then passed through the glass plate, and so through the analyzing nicol. The reflecting surfaces could be adjusted exactly at right angles to the direction of the incident rays of light, and as nearly as possible at right angles to the axis of the electromagnet, by observations for the purpose.

The plane of polarization of the polarizing nicol was made to coincide as exactly as possible with the plane of incidence, in order to have as much light as possible. If upon reflection from the metallic surface any rotation took place, so that the plane of polarization of the reflected light no longer coincided with the plane of incidence upon the glass plate inclined at 45°, then upon passing through this a further rotation took place corresponding to Fresnel's formula for the refraction of polarized light. The analyzing nicol is therefore used to measure, not simply the electromagnetic rotation at the metallic surface, but the sum of this and the rotation produced by the glass plate. The latter, of course, was placed so far from the magnet that no electromagnetic rotation could be produced in it.

If α denote the angle which the plane of polarization of a ray of light falling upon a glass plate makes with the plane of incidence, then the angle γ between the two planes, after passage through the plate, is given by the formula

$$\tan \gamma = \frac{\tan \alpha}{\cos^2 (i-r)},$$

where i and r denote the angles of incidence and refraction respectively.

Since in the observations i was always nearly 45° and the refractive index of the glass about 1·48, calculation shows that the values of the directly observed rotations must be decreased by about 10 per cent. in order to obtain the actual electromagnetic effect. Dr. Kerr as well as Mr. Gordon seem to have overlooked the effect of the glass plate; at least they do not mention it.

I have retained the same arrangement of the glass plate as these observers, that it might be possible to have the light

actually falling upon the metallic surface exactly at right angles.

Mirrors of iron, cobalt, and nickel were used for these experiments, prepared by electrolytic deposition of the metal upon platinized glass. It has already been remarked that in consequence of the small thickness of these plates, the forces exerted upon them by the magnets are so small that no distortion of the glass plates which support the metal films can occur.

Iron.

Four mirrors were employed.   Rotation.

No. 1. Iron film so thick as to be com- }
       pletely opaque . . . . . . } $-53'\cdot6$

No. 2. Transparent . . . . $-45'\cdot4$

No. 3. Transparent . . . . $-1°\,5'\cdot8$

No. 4. Transparent . . . . $-48'\cdot8$

The rotation is opposite to the direction of the magnetizing current; consequently the above numbers, like the following ones for cobalt and nickel, are marked with the negative sign. It must be mentioned that a dispersion due to rotation was distinctly observed in reflection also, which, like that produced by the transmission of light, is an anomalous dispersion—*i. e.* the red rays are rotated more powerfully than the blue ones. It is remarkable that mirror No. 3, which was very transparent, shows so large a rotation. I have noticed several times that other mirrors, also of smaller thickness, have shown a comparatively large rotation. I have not yet been able to make more accurate experiments on the connexion of the rotation with the thickness of the reflecting layer.

Cobalt.

Three cobalt mirrors were examined.

No. 1. Transparent, gave a rotation of . $-1°\,7'\cdot2$

No. 2. Hardly transparent,   „ $-\ 50'\cdot9$

No. 3. Opaque,   „ $-\ 50'\cdot3$

Here also a feeble dispersion due to rotation could be observed.

Nickel.

Of two mirrors which were examined,

No. 1. Transparent, gave a rotation of . $-20'\cdot5$

No. 2. Opaque   „ $-23'\cdot0$

Thus nickel, upon reflection, rotates only about half as powerfully as iron and cobalt. Moreover, as was shown above, the rotation of transmitted light produced by nickel is perceptibly smaller than that due to iron and cobalt.

The molecular condition of the surface must undoubtedly play an important part in reflection; and since this may vary very greatly with the concentration of the solution and the strength of the current, it is hardly to be expected that identical values should be obtained for the rotation of different mirrors. In order to obtain the electromagnetic rotation alone, all the values given above must be diminished by about 10 per cent.

In conclusion, it may further be mentioned that I have also coated platinized glass with iron and then electroplated the iron with silver or copper. These iron mirrors covered with silver or copper showed no perceptible rotation upon reflection. If we adjust matters so that the rays fall accurately vertically upon the metallic surfaces, the glass plate may be dispensed with, replacing it by a perforated mirror of non-magnetic metal, and adjusting it so that the reflected light passes through the hole into the eye of the observer. The rotation observed with this arrangement is produced by reflection at the magnetized mirrors between the poles.

V. *Refutation of* Fitzgerald's *Theory of Rotation produced by Reflection.*

Mr. Fitzgerald * has endeavoured to give an explanation of the rotation of the plane of polarization produced by reflection. Briefly stated, it is as follows:—Iron, upon magnetization, becomes circularly doubly refractive, just as diamagnetic substances in a magnetic field do. This circular double refraction, as has been shown above, is very considerable in the case of iron. Since the intensity of the light reflected by a body depends upon its index of refraction, right-handed circularly polarized light is reflected by magnetic iron with a different intensity from left-handed. Plane-polarized light may be regarded as consisting of equal quantities of right-handed and left-handed circularly polarized light. Starting from this point, Fitzgerald endeavours to show that plane-polarized light falling at any angle upon a magnetic surface is converted by reflection into elliptically polarized, and that in general the major axis of the ellipse must be rotated towards the direction of oscillation of the incident light. For *normal* incidence upon the pole of a magnet, however, it is easily seen that the angle between the plane of oscillation of the incident light and the major axis of the ellipse is zero. Mr. Fitzgerald therefore himself draws the following conclusion from his theory:—If plane-polarized light falls normally upon the pole of an electromagnet not excited, and if after reflection it be

* Proceedings of Royal Society, xxv. p. 447.

quenched by a nicol, then upon exciting the electromagnet the field should become bright. This brightness should not disappear upon any rotation of the analyzing nicol, but should increase, whether it be rotated to the one side or to the other.

To this my experiments are directly in opposition; inasmuch as, when the electromagnet was excited, the analyzing nicol had always to be rotated through a definite angle in order to obtain good extinction. Whether the extinction itself is *absolute* with homogeneous light, and consequently whether the reflected light remains strictly plane-polarized or whether a certain *small amount* of ellipticity results, cannot of course be decided. In any case Fitzgerald's theory is refuted by the experiments at normal incidence, and it is therefore not necessary to discuss the admissibility of the assumptions upon which it is based. The question how far Voigt's theory on the reflection of light at circularly polarizing media is applicable to our case may remain undecided for the present.

VI.

Rotation of the Plane of Polarization upon Oblique Reflection of Light from the pole-surfaces and side-faces of a Magnet.

For these experiments a large electromagnet with erect legs of iron was employed. These had a height of 47 centim. and a diameter of 11 centim. Each leg was provided with three coils of wire 3 millim. thick : each coil had a resistance of about 0·65 Siemens unit. Two large iron parallelepipeds served as poles. The magnetizing current was furnished by the Gramme machine, and had usually an intensity of 16 amperes. Since the experiments were made in winter, when the sun was little to be relied upon, a Drummond lime-light was employed as source of light. The readings of the analyzing nicol were taken upon a divided circle graduated into quarter-degrees, reading with the vernier to 4 minutes, although the reading could be estimated to 2 minutes with certainty.

The angle of incidence of the rays of light upon the reflecting iron surface was carefully read off upon a divided circle. The plane of polarization of the polarizing nicol was adjusted as exactly as possible in the plane of incidence or at right angles to it, as determined by the good extinction of the light by the analyzer. When the magnet was excited, it was generally not possible to get rid of the light which now passed by rotation of the analyzer; since after reflection the light was no longer plane-polarized, but elliptically polarized. It was always adjusted to the minimum of illumination, so that the plane of oscillation of the analyzing nicol was brought at right angles to the long axis of the rotated elliptical rays.

Since the rotations are very small in amount, it was necessary, in order to obtain results in any measure reliable, to multiply the observations. As a rule, four observations were taken for each angle of incidence, for each of the two positions of the plane of polarization, viz. in the plane of incidence and at right angles to it. In each of the four observations the polarizer was adjusted afresh, and ten readings taken with each direction of the current. In the following a rotation is called positive, as before, when it has the same direction as the projection of the amperian molecular currents upon a plane at right angles to the ray of light.

First Series of Experiments.

A circular iron mirror, of the dimensions given above, was employed. The iron pole-pieces were adjusted at a distance of 29 millim. from each other, and maintained at this distance apart by means of a block of wood inserted between them. The mirror was placed sideways upon the magnet-poles, so as to touch each through a distance of 3 millim. The magnet was thus closed through the steel mirror. The reflecting surface was placed vertical. The angle of incidence J is the angle between the incident rays and the normal to the mirror.

The following Table gives the results obtained. The sign = denotes that the plane of polarization (the long diagonal of the nicol) is parallel, and the sign $\perp$ that it is at right angles to the plane of incidence.

The amount of rotation is given in minutes. Since each number is the result of eighty separate adjustments, the tenths of minutes are given, although the error may amount to several tenths of a minute.

J.		=	$\perp$
$19^\circ{\cdot}0$	....	$-4{\cdot}8$	$+2{\cdot}7$
$29{\cdot}9$	....	$-4{\cdot}5$	$+7{\cdot}3$
$39{\cdot}5$	....	$-6{\cdot}6$	$+7{\cdot}7$
$50{\cdot}1$	....	$-7{\cdot}7$	$+6{\cdot}9$
$61{\cdot}3$	....	$-8{\cdot}0$	$+7{\cdot}5$
$65{\cdot}0$	....	$-9{\cdot}4$	$+8{\cdot}7$
$70{\cdot}0$	....	$-7{\cdot}1$	$+8{\cdot}1$
$75{\cdot}0$	....	$-6{\cdot}0$	$+6{\cdot}8$
$80{\cdot}3$	....	—	$+2{\cdot}6$
$82{\cdot}0$	....	$-4{\cdot}3$	$-2{\cdot}3$
$85{\cdot}2$	....	$-3{\cdot}9$	$-1{\cdot}9$

These experiments completely confirm Kerr's results—that

for the position of parallelism the direction of rotation is the same for all incidences and opposed to the molecular currents, while when the planes are at right angles the rotation changes sign for an angle of about 82°.

Our experiments also show a maximum rotation at 65°, as Kerr gives.

Second Series of Experiments.

An exactly similar series of experiments was made with a steel mirror of the same size, whose surface had been electroplated with nickel. The following values were obtained :—

J.	=	⊥
20·0	0·0	+0·0
30·1	−1·7	+1·8
40·0	−2·7	+1·4
50·0	−4·7	+0·3
61·5	−4·2	−0·7
65·3	−3·8	−2·2
75·0	−1·1	−1·9

With nickel also the direction of rotation remains the same for all incidences =, but for the position ⊥ changes its sign between 50° and 60°.

The amount of rotation is, on the whole, perceptibly smaller than with iron. This is in agreement with what was said above as to the ratio of the rotatory power of nickel to that of iron.

In order to test whether any perceptible distortion or bending took place when the magnet was excited, the images of a vertical and horizontal millimetre-scale were observed by means of a telescope in the manner already described. When the current was established, there occurred always a very slight displacement, and also a small bending of the mirror. The latter was inferred from the fact that the divisions and numbers of the scale between became somewhat indistinct. These displacements and distortions were, however, extremely slight; and the same whether the current was sent in the one direction or in the opposite. They could not therefore have exerted any perceptible effect upon the observed rotations. Besides the complete series of observations described, a large number of separate observations were made with the various mirrors under various conditions. They were all in complete agreement with the numbers of the above tables. The following may be quoted :—

Another steel mirror, similar to the one used for the series of experiments, gave at an angle of incidence of 65°·3,

$$\overset{=}{-8'·6} \qquad\qquad \overset{\perp}{+9'·0}$$

This mirror was then electroplated with silver. Upon establishing or reversing the current there was no perceptible brightening of the field.

The pole-pieces of the magnet were then put into contact, and the mirror which was to be examined was placed at the side of the magnet, but without touching it. For this purpose mirrors of non-magnetic metal and platinized glass were employed which had been electrolytically coated with a thin film of iron. An accurate examination of the same by means of the scale and telescope showed not the smallest displacement or distortion when the magnet was excited. A rotation was observed in every case, as was to be expected from the results given in the above tables. Thus, for example, a glass mirror coated with iron gave for an angle of incidence of 65°, when the iron-coated side was about 2 millim. from the side of the magnet, the following rotations:—

$$\overset{=}{-8'·1} \qquad\qquad \overset{\perp}{+13'·0}$$

A rotation could still be observed when the mirror was at a distance of 45 millim. from the side surface of the magnet.

I have made also a number of experiments on the rotation produced upon oblique incidence on the end faces of a magnet. The arrangement was the same as that employed by Kerr. Platinized glass coated with iron, cobalt, or nickel was used in every case. The mirror was fastened in front of the plane-pole of an electromagnet without touching it, and a pointed pole (submagnet of Kerr) brought near to the mirror. If the plane of polarization coincided with the plane of incidences, then for all incidences the direction of rotation is opposed to that of the magnetizing current if we imagine the reflected ray of light rotated in the line joining the poles.

If the plane of polarization is at right angles to the plane of incidence, then at an incidence of about 80° the rotation is also oppositely, but from 80° to 90° similarly, directed with the magnetizing current. This reversal in the direction of rotation, as already remarked, escaped Kerr's notice. Since I have not yet been able to make a complete series of observations with one and the same mirror on the variation of rotation with the angle of incidence, I defer giving numbers for the present.

VII.

Rotation of the Plane of Polarization of Light which has twice traversed a glass plate and been reflected at the back surface of the plate.

The phenomena of reflection of light from metals have led to the view that the light upon reflection penetrates into the metal to a certain depth. This easily suggests the suspicion that the rotation of the plane of polarization of light which has suffered reflection from magnetic metallic surfaces arises in the very thin layer which the rays traverse upon reflection. A theory of rotation upon the assumption of the penetration of the light would be difficult to establish.

We may, however, easily state matters so that, in general at least, a process takes place analogous to that of reflection at metallic surfaces, upon the assumption of the penetration of light. Suppose that we have a glass plate in a magnetic field : let rays of light fall upon it at any angle of incidence. The rays are refracted into the glass, traverse the plate, are reflected at the back surface, and after traversing the plate a second time are refracted out of the glass.

If we have the amount of the electromagnetic rotation of the rays by glass given, then, by help of Fresnel's formula for reflection and refraction in isotropic bodies, the total rotation which the plane of polarization has suffered in the plate can be calculated. We will consider the following special case, which is analogous to our previous experiments on rotation at the side-faces of a magnet.

Let the lines of force of the magnetic field in which the glass plate is placed be parallel to the plane of the plate. Let the thickness of the plate be d, and the electromagnetic rotation per unit length in the direction of the lines of force be ϕ. Let the plane of polarization of the incident light coincide with the plane of incidence, and be parallel to the lines of force. Then, if Fresnel's formula for refraction at the first surface and reflection at the second surface be employed, the angle γ through which the plane of polarization is rotated upon emergence from the plate—if i and r represent the angles of incidence and refraction, and if the electromagnetic rotation in the plate is so small that the angle, its tangent, and its sine may be considered identical—is given by the formula

$$\tan \gamma = 2\phi d \tan \gamma \frac{\sin i \sin r}{\cos^2 (i-r)}.$$

Since all the factors of ϕ are positive, γ has the same sign as ϕ for any value of i. For $i=0$, $\gamma=0$. The rotation of the

plane of polarization which the glass plate shows upon excitation of the magnetic field thus varies, no doubt, in magnitude with the angle of incidence, but always takes place in the same direction as the electromagnetic rotation which the rays suffer in the plate.

If, on the other hand, the plane of polarization of the light before its entry into the plate is at right angles to the plane of incidence, if we adopt the same symbols, and if the electromagnetic rotation is again small, then the rotation x, suffered by the plane of polarization upon emergence from the plate, is given by the formula

$$\tan x = -2\phi d \tan \gamma \, \frac{\sin i \sin r \cos (i-r)}{\cos (i+r)}.$$

If $i+r < 90$, x is negative; but if $i+r > 90$, x is positive.

For $i+r = 90$, that is, for the polarizing angle, $x = 90$; but in this case the amplitude of the light is zero.

The case considered above was examined experimentally in the following manner:—The poles of the large electromagnet were adjusted at a distance of about 3 centim. apart. A glass plate, the walls of which were not accurately parallel, so that the rays reflected from the back surface were well separated from those reflected at the front surface, was placed against the vertical side-faces of the poles so that it connected them. The plane of incidence of the light was horizontal. The angles of incidence were read off upon a large divided circle.

The following double rotations were obtained upon exciting the electromagnet at different angles of incidence for the rays reflected at the back surface.

The signs $=$ and $\perp$ denote, as before, that the plane of polarization of the incident light is parallel or at right angles to the plane of incidence. The rotations are given in degrees.

Angle of incidence.		Rotation.
	$=$	
$50°5$	....	$+0°8$
$61·3$	....	$+1·6$
$70·0$	....	$+2·5$
$80·4$	....	$+3·4$
	$\perp$	
$30°7$	....	$-\ 0°7$
$39·5$	....	$-\ 1·8$
$50·5$	....	$-\ 4·8$
$53·8$	....	$-27·4$
$60·4$	....	$+24·1$
$61·3$	....	$+12·0$
$70·0$	....	$+\ 6·2$
$80·4$	....	$+\ 4·2$

The polarizing angle of the glass ($i + r = 90°$) was found to be $56°\cdot4$.

A similar series of experiments was made, with the two poles of the electromagnet pushed close together and the glass plate placed against the side surface of the closed magnet.

The rotations were similar to those given above. There is consequently a complete analogy between the phenomena obtained with the glass plate and the previously given observations of reflections at the side-faces of a magnet.

In that case, as in this, when the plane of incidence and the plane of polarization coincide all rotations have the same sign. If, however, the plane of polarization is at right angles to the plane of incidence, then, with metals as with glass, the sign of the rotation changes—for glass at the polarizing angle ($56°\cdot4$), for iron at about $80°$, for nickel at about $60°$.

Nevertheless we have the difference that, with the magnetic metals the direction of rotation is the opposite to that in the case of glass. If it is not allowable to assume that it is proved by this analogy that, upon reflection at metallic surfaces, the light penetrates to a small depth into the metal, and that the rotation takes place in the thin layer which the reflected rays traverse, yet the phenomena of rotation observed upon reflection at the side of a magnet admit of being brought under a simple and uniform expression. The fact that the light rotated upon oblique incidence on metals does not preserve its condition of plane polarization, but becomes elliptical, has been shown above.

Instead of bringing our glass plate up to the side-face of a magnet, we may bring it in front of the pole-surfaces so that the lines of force are at right angles to it. The amount of the rotation of the plane of polarization when the magnet is excited may be calculated as a function of the angle of incidence and position of the plane of polarization by means of Fresnel's formula, as explained above. The result is that, when the plane of polarization of the incident light lies in the plane of incidence, the rotation always has the same sign, viz. positive ; but when the plane of polarization is at right angles to the plane of incidence, then from $0°$ up to the polarizing angle the rotation is positive, and thence on to $90°$ it is negative.

These phenomena are therefore exactly analogous to those of rotation at the pole-surfaces of a magnet, with the difference that we must ascribe a negative power of rotation to the magnet.

VIII.

In the preceding I have given a general view of the electromagnetic rotation of iron, cobalt, and nickel upon transmitted and upon reflected light. A more exact investigation of the dispersion due to rotation, of the dependence of rotation upon the thickness of the layers in reflection, &c., must be reserved for a subsequent occasion. Other questions suggest themselves : as, for example, whether the rotation attains its maximum with the induced magnetic moment, whether it is possible to recognize a rotation produced by a thin metallic film, which is permanently magnetized instead of being temporarily magnetized, &c.

I will here, in conclusion, only collect together the facts now known of the electromagnetic rotation of the plane of polarization. We will, as usual, designate a rotation in the direction of the hypothetical amperian molecular currents, which represent at the place in question the magnetic field actually present as *positive*, and an opposite rotation as *negative*.

1. Most isotropic solid bodies, fluids, and those gases which have been examined rotate the plane of polarization in the positive direction.

2. A concentrated solution of ferric chloride produces a negative rotation. The negative rotation of other magnetic salts is recognized by the diminution in the positive rotation of the solvent.

3. Oxygen, which is comparatively powerfully magnetic, produces positive rotation, as shown by Herr Röntgen and myself.

4. The plane of polarization of light which traverses iron, cobalt, and nickel is rotated in the positive direction.

5. According to Kerr, negative rotation is produced upon normal reflection from a magnetic pole. The same has been shown above to hold good for cobalt and nickel.

6. Upon passing through, as well as upon reflection from, iron, the rotational dispersion of the light is anomalous—that is, red rays are rotated more powerfully than blue ones.

7. The complicated phenomena which take place upon oblique reflection from the pole-surfaces, or side-faces of a magnet, may, as shown above, be brought together by the assumption that, in reflection, the light traverses a very thin film of the metal, and that negative rotation is produced by this layer.

XXXVI. *Experiments on the Velocity of Sound in Air.* *By* D. J. BLAIKLEY[*].

[Plate VII.]

I HAVE to bring before you this afternoon the results of a few experiments carried out in continuation of the series brought to your notice last November. Before considering the velocities obtained, however, it may be well to show by experiment the reason for the doubt in my mind as to the absolute reliability to be placed upon records obtained from membranes as used by Regnault and Le Roux; and also to explain a little more fully my reason for discarding the use of organ-pipes, speaking under a considerable pressure and with good musical tone, as used by Dulong.

If we take a short tube, say 5 inches long, with a short inner sliding-piece for adjustment of length, and close one end with a diaphragm of gold-beater's skin, against which a bead hung by silk falls, we have a very sensitive resonator for the pitch of about 512 v. If this tube were closed by a rigid material instead of by the skin, its length to give the maximum resonance to the 512 v. fork would be about $6\frac{1}{4}$ inches; but on drawing the slide to make the tube of this length there is no agitation of the bead : the maximum agitation of the bead, at the present tension of the membrane, is found to be when the tube is about 5 inches long. This is its most sensitive position ; but when the fork is vibrating strongly the membrane will record its action, although the length of the tube, from mouth to membrane, is somewhat greater, or less, than is necessary for best effect. Applying this to the case of a membrane stretched across a tube along which a single wave is travelling, as in Regnault's experiments, it would appear that the last possible record of the enfeebled wave would be obtained from its point of maximum condensation ; but a record of the wave in the early part of its course, when it is strong, would be obtained from a point in the wave far short of its maximum condensation ; so that the length measured by means of the membranes, as travelled by the wave, does not necessarily give the length passed over by a given point in the wave in the measured time. The error, small as it would be when distributed over a great length, would become more appreciable as the tube-length became shorter, and it would in every case lead to an under-estimation of the velocity.

In Dulong's experiments care was taken to obtain pipes of good tone ; but my experiments have convinced me that such a tone is the worst possible for measurement of wave-lengths. A good musical tone is not pure in the acoustical sense, and the presence of the partials constrains the pitch of the prime to some extent. If the form of pipe were such that its proper tones agreed exactly with the harmonic series, there would not be this difficulty of constrained pitch ; but as it would have been exceedingly difficult to construct pipes of this character, I determined to introduce a bulb or pear-shaped portion between the speaking-mouth and the cylindrical tube in which the sliding-plug worked (see Plate VII. fig. 1). By this means tubes were obtained having proper tones quite out of the harmonic order, and therefore capable of giving very pure prime tones.

In November last it was stated that the results obtained from the 11·43 millim. tube were not very reliable. The experiments with this tube have been repeated, and a new tube of 88·19 millim. diameter has been introduced, completing a series of five tubes, ranging in the proportion of 3 to 5, from 11·43 to 88·19 millim. diameter*. The results of the new experiments are given in the following table :—

TABLE IV.

Velocity of Sound in dry Air, at 0° C., in tubes.

Diameter of tube	11·43 millim.	88·19 millim.
	324·533	330·29
	324·234	330·46
		330·02
		329·72
		329·99
		330·41
		330·09
		330·06
		330·10
		330·20
Means	324·383	330·134

In Table V. the results of all the experiments are brought together :—

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* Through a clerical error the diameters of the tubes were previously given as 11·7, 19·5, 32·5, and 54·1 millim., instead of 11·43, 19·05, 31·71, and 52·91.

TABLE V.

Radius, in metres......	r ·005715	r_1 ·009524	r_2 ·015874	r_3 ·026457	r_4 ·044095
Velocity at 0° C., in metres	v 324·383	v_1 326·902	v_2 328·784	v_3 329·723	v_4 330·134
Mean pitch during observations	n 322·96	n_1 260·36	n_2 260·18	n_3 172·48	n_4 131·15
$\sqrt{\dfrac{1}{n}} \cdot \sqrt{\dfrac{1}{n_1}}$ &c. ...	·05563	·06197	·06200	·07615	·08732

From these data we may obtain a value for V = velocity in free air, where $r = \infty$, using a modification of the formula

$$v = V\left(1 - \frac{\alpha}{r}\right). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The formula $v = V\left(1 - \dfrac{\alpha}{r}\right)$ gives only a fictitious value for v when r is very small; whereas v should $= 0$ when $r = 0$, and should $= V$ when $r = \infty$.

Put F for the ratio $\dfrac{v}{V}$, and f for $(1 - F) = \dfrac{V - v}{V}$. Then, when $v = 0$,

$$F = 0 \text{ and } f = \frac{V}{V} = 1 ;$$

and when $v = V$,

$$F = 1 \text{ and } f = 0.$$

When $F = 0$,

$$\log \frac{1}{F} = \infty ;$$

when $F = 1$,

$$\log \frac{1}{F} = 0.$$

Therefore in (1), where

$$\frac{\alpha}{r} = \left(1 - \frac{v}{V}\right) = (1 - F),$$

make

$$\frac{\alpha}{r} = \log \frac{1}{F} = \log \frac{V}{v} = \log V - \log v,$$

or

$$r\left(\log \frac{V}{v}\right) = r_1\left(\log \frac{V}{v_1}\right). \quad . \quad . \quad . \quad . \quad (2)$$

In (1)
$$\alpha = \sqrt{\frac{\mu}{2np}}$$

(Lord Rayleigh, 'Theory of Sound,' § 347),

$$= \sqrt{\frac{\mu}{2p}} \cdot \sqrt{\frac{1}{n}},$$

so that

$$\left(\alpha - \sqrt{\frac{\mu}{2p}}\right) \propto \sqrt{\frac{1}{n}}.$$

As a slight deviation from accuracy in the relative values of $\sqrt{\frac{1}{n}}$ would affect the calculated values of V only to an exceedingly small extent, we may put

$$\sqrt{\frac{1}{n}} = \cdot 9, \quad \sqrt{\frac{1}{n_1}} = 1, \quad \sqrt{\frac{1}{n_2}} = 1, \quad \sqrt{\frac{1}{n_3}} = 1\cdot 2,$$
$$\text{and } \sqrt{\frac{1}{n_4}} = 1\cdot 4$$

in place of the values given in Table V.; and introducing these values into formulæ (1) and (2), we get

$$\frac{1\cdot 4}{r_4} = \log\frac{V}{v_4}; \quad \frac{1\cdot 2}{\frac{3}{5}r_4} = \log\frac{V}{v_3}, \text{ &c., &c.,}$$

or

$$\log V = \frac{10 \log v_4 - 7 \log v_3}{3}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

From which
$$V = 331\cdot 089.$$

In the same way values for V can be found from any two values of v—as v and v_1, v and v_4, &c., as follows :—

TABLE VI.

	v_4 and v_3	=	$331\cdot 089$
	v_3 ,, v_2	=	$332\cdot 150$
	v_2 ,, v_1	=	$331\cdot 620$
	v_1 ,, v	=	$331\cdot 999$
V as obtained from	v_4 ,, v_2	=	$331\cdot 508$
	v_3 ,, v_1	=	$331\cdot 881$
	v_2 ,, v	=	$331\cdot 746$
	v_4 ,, v_1	=	$331\cdot 540$
	v_3 ,, v	=	$331\cdot 620$
	v_4 ,, v	=	$331\cdot 603$

Mean . . . $= \overline{331\cdot 676}$

As v_1 and v_2 have practically the same values for n, V as obtained from this pair of velocities is uninfluenced by the

Z 2

factor $\sqrt{\dfrac{1}{n}}$; and if the influence of n is properly represented by $\sqrt{\dfrac{1}{n}}$, the mean of all the values of V should agree with V as obtained from v_1 and v_2. The mean is 331·676 metres; and the latter value is 331·620, with which the mean is in very close agreement. The pairs of adjacent values v_4 and v_3 &c. are rather ill-conditioned for the determination of V: the best value of V should be from the extreme values of v—that is, the pair v_4 and v. This value is 331·603—very little different from the value 331·620 obtained from v_2 and v_1, where there is no variation in the value of $\sqrt{\dfrac{1}{n}}$. From these results it would appear that the influence of the vibrational rate of stationary waves in tubes upon the velocity is properly represented by $\sqrt{\dfrac{1}{n}}$; but as Lord Rayleigh, in the paragraph quoted, refers to Schneebeli's and A. Seebeck's investigations, based upon Kundt's experiments, we may calculate a value for V upon their determinations. According to these observers, when n varies, the diminution of velocity is proportional rather to $\sqrt{\dfrac{1}{n^3}}$ than to $\sqrt{\dfrac{1}{n}}$. Taking the pair of velocities v and v_4, and substituting $\sqrt{\dfrac{1}{n^3}}$ for $\sqrt{\dfrac{1}{n}}$, we get V = 334·439—manifestly too high, and very different from 331·620, the value obtained from the pair v_1 and v_2.

In the diagram (Plate VII.) and in Table VIII. I have therefore used $\sqrt{\dfrac{1}{n}}$; but this, or any modification of it such as $\sqrt[n]{\dfrac{1}{n^m}}$, can only be applicable, and then but approximately, within certain limits.

TABLE VII.   TABLE VIII.

Calculated velocity, in metres, at the pitch of 260 vibrations.	Comparison between values of v, v_1, v_2, v_3, v_4, as observed and as calculated, at the pitch of observation s, V being taken as 331·676 metres.						
	Radius.		Velocity, in metres.		Differences.		n, or pitch.
			Observed.	Calculated.	−	+	
323·728	r	·005715	v	324·383	324·514	...	·131	322·96
326·884	r_1	·009524	v_1	326·902	326·884	·018	...	260·36
328·792	r_2	·015874	v_2	328·784	328·792	...	·008	260·18
329·943	r_3	·026457	v_3	329·723	329·545	·178	...	172·48
330·635	r_4	·044095	v_4	330·134	330·209	...	·075	131·15

In the diagram (Plate VII.) the curve given by the figures in Table VII. is laid down, and also the observed and calculated values given in Table VIII. To these are added curves for 130, 520, and 1040 vibrations.

In addition to the experiments of which the details are given, many trials were made in the course of adjusting the apparatus. Some of these trials were at pitches other than those finally adopted; and although such results were of no value for exact comparison, the general bearing of them was quite in agreement with the results tabulated. One of these preliminary trials was a set of five observations with the tube of 52·91 millim. diameter (r_3) at the pitch of 260. The mean result was a velocity of 330·27, in place of 329·94 as on Table VII. This trial was made with the tube before the introduction of the bulb-mouth; and the third partial tone was perceptible to the ear, so that the prime may have been influenced a little thereby.

The notes were all purposely kept very weak, so that the excess of pressure in the tubes when sounding, above the barometric pressure, must have been very small indeed. In one of the large tubes (r_3) a water-pressure gauge was introduced; but the pressure was barely measurable, certainly not exceeding $\frac{1}{50}$ inch of water. In the calculations I have therefore assumed that the influence of intensity might be neglected.

The chief conclusions to which these experiments appear to lead are the following:—

1st. The tubes used for the measurement of wave-length, as determined by the length between nodes, must speak with a pure tone; or

2nd. If partials are present, the tubes must be of such form as to have their proper tones in exact agreement with the harmonic series. (Neither of these conditions is easily attainable with ordinary organ-pipes.)

3rd. The air-blast must not constrain the pipe to speak any other pitch than its natural pitch of resonance.

4th. In smooth tubes the diminution of velocity is proportional to r^{-1} and to $n^{-\frac{1}{2}}$, as determined by Helmholtz.

5th. The velocity V in free air for sound-waves of low intensity, or just audible, is 331·676 metres at 0° C.

6th. The ratio between the two specific heats of air, as deduced from the Newtonian velocity 279·955 metres, and V as above 331·676 metres, is 1·4036.

As there is perhaps room for some doubt about the influence of n being properly represented by $n^{-\frac{1}{2}}$, I have not attempted

to employ Kirchhoff's equation in place of Helmholtz's ; but in abler hands than mine, the experimental results may perhaps be of some assistance in determining one or more of the points involved in these formulæ.

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XXXVII. *On the Surface Forces in Fluids.*
By A. M. Worthington, *M.A., Clifton College, Bristol* *.

[Plate VIII.]

1. THE object of the following paper is to deduce from consideration of the internal equilibrium of fluids the fact that at their bounding-surface there is a rapid variation of density, on account of which the surface layers exert either a tension or a pressure on any material wall which cuts them transversely, from which action all the known phenomena of capillarity are easily deduced ; and to exhibit clearly the manner in which the intrinsic energy per unit of volume of the surface layers exceeds or falls short of the intrinsic energy of the unit of volume in the interior of the liquid ; and also to point out a certain important change which it is necessary to introduce into the commonly accepted explanation of the equilibrium of a fluid in contact with a solid ; and, finally, to show why the erroneous assumption by Laplace of a constant density near the surface did not prevent him from obtaining the correct equation to the liquid surface.

That a variation of density will usually take place at the surface of a liquid was indeed admitted by Laplace† ; but the variation was not taken into consideration in his theory, nor was its significance perceived by him, but seems first to have been pointed out by Poisson‡, in whose investigation all necessary considerations are taken into account. But the methods of Poisson leave much to be desired in point of simplicity and directness ; aud to many readers the issue must appear unnecessarily obscured by mathematical difficulties. Moreover, he did not realize—perhaps it was impossible before the researches of Quincke that any one should realize— that the one quantity which alone we can measure experimentally is a surface-tension ; and consequently he did not aim at proving the reality of its existence. Yet the argument which I shall make use of follows so naturally from the considerations adduced in his chapter " Sur la Constitution intime des

Corps," that it may be said to be founded upon the ideas which are there so lucidly set forth.

Before the development of the modern theory which ascribes the phenomena of heat to molecular motion, it was customary to regard a solid or liquid at rest as composed of an indefinitely large number of discrete molecules, themselves also at rest; and physicists, such as Young and Poisson, did not hesitate to frame theories which should account for the statical equilibrium of such molecules. The phenomena of cohesion and adhesion required that the molecules should be endowed with an attractive force which was a function of the distance between them, and which vanished when the distance became sensible; while the phenomena of elastic resistance to compression, and of expansion with a rise of temperature, led to the description of a repulsive force of heat which was supposed to be exerted between adjacent molecules. The molecules of a homogeneous solid were supposed to be of equal mass and of equal efficiency as centres of force, and to be uniformly distributed throughout the interior of the solid. A varying state of stress corresponded to variations from uniformity in the arrangement of the molecules, while fluids were distinguished from solids by the supposition that the internal equilibrium of the latter was influenced by the shape as well as by the situation of the molecules; while in the case of the former, owing either to the sphericity of the molecules or to their relatively great distance of separation, consideration of their shape was unnecessary.

The properties ascribed to the molecules were those which seemed simplest, or which were most obviously suggested by analogy with phenomena in which finite masses of matter were concerned. No attempt was made to explain how the molecules acquired these properties of attracting or repelling each other at a distance.

The properties must not, however, be regarded as so many additional hypotheses about the molecules, but rather as a part of the conception of stationary molecules, which observation of phenomena proved to be necessary.

A large number of phenomena, however, especially those belonging to gaseous pressure, diffusion of gases and liquids, and to evaporation, were not explainable by the supposition of stationary molecules, but seemed to demand that they should be regarded as endowed with motion; and this opinion, which received so great an encouragement from the discovery of the mechanical equivalent of heat, is now almost universally accepted.

But the change of the point of view has, as is often the

case, its disadvantages as well as advantages. A multitude of phenomena of the classes mentioned receive an easy explanation; but the explanation of others has become more troublesome than before. The mere mathematical difficulty of dealing with a number of molecules in motion renders it impossible, on the supposition of molecular motion, to frame a satisfactory theory of internal equilibrium in solids or liquids. We are obliged therefore either to invent new methods, or to return to the old point of view; and it is important therefore, while the more energetic minds are inventing new statistical methods of dealing with molecules and substituting the new conception of a transfer of momentum for the old one of a "force," to examine the statical theory to ascertain whether a perfectly philosophical use may not be made of it. For it often happens, in the observational sciences, that the hypotheses of one theory are completely represented in corresponding hypotheses of another theory, and that the results of the one can be translated into the language of the other; so that an impartial observer will regard the hypotheses of either rather as conventions between which there may indeed be some choice on the ground of convenience and suitability, than as statements of fact whose truth or falsehood is at issue. Now, it is easy to see that the relation between the statical and dynamical molecular hypotheses is one of this kind, and that to the properties which we assign to the molecules on the one theory there are corresponding properties assigned on the other.

Thus, in either, the molecules are regarded as attracting each other with a force which is a function of the distance only, independent of the temperature and vanishing when the distance becomes sensible. On the statical theory the molecules are supposed to be kept apart by a repulsive force which varies with the temperature, and which is also a function of the distance, but which turns out to be exerted only between adjacent layers of molecules. On the dynamical theory the equivalent property is the motion itself, combined in some forms of the theory with an elastic repulsion between molecules in collision, causing them to separate again (various subordinate hypotheses having been suggested to account for this latter property). And the explanation of the difference in molecular structure between fluids and solids offered on the one theory also corresponds closely with that belonging to the other.

And, again, it is significant to observe that, so far as the internal equilibrium of substances is concerned, the conception of molecular motion stands in the same relation to the statical conception as the modern theory of a dielectric does

to the earlier notion of action at a distance between electrified bodies. For, on the statical theory, we regard the equilibrium of any two parallel layers of uniformly distributed molecules, sufficiently near to act upon each other, as maintained by forces of attraction and repulsion acting across the empty intervals which separate them from the intervening molecules; while, on the dynamical theory, we account for the latter of these two forces by what is equivalent to a pressure arising from the momentum of these intervening molecules, which thus constitute a medium the action of which replaces one of the actions at a distance; and it is well known that in the case of electricity the results of the earlier theory are all trans-latable into the language of the later.

And it is pertinent also to remember that it is a common artifice in dynamical problems, as for instance in Planetary Astronomy, to make abstraction of the motion of a portion of the system by the introduction of a repulsive force. In the present instance the whole system probably consists of a number of molecules in motion which, being endowed with attractive forces, would, but for their motion, fall together. If we are to imagine them stationary, and at the same time to preserve the external characteristics of the system, we must introduce the repulsive forces.

I have thought it well to preface the argument which follows by these remarks, since there is a tendency to forget or disregard results obtained by the statical theory, because the language in which they are expressed is thought to be out of harmony with the newer conceptions.

In the arguments which follow it will be found that, while dealing with solids and liquids, I have preferred to use the conception of separate molecules, and to speak of the intra-molecular distances as decreasing or increasing with the application of external pressure or tension, though the argu-ments would equally well have permitted me to speak of elementary volumes and variations of density: in fact, that it is not till the subject of gases is considered that it becomes necessary to speak of molecules. It appears to me, however, that, apart from the desirability of adopting through-out the paper the same system of describing phenomena, there is an advantage in choosing a method which shows that the conclusions arrived at in the case of solids and liquids are consistent with the assumption of molecular discontinuity, should it be necessary to make that assumption.

2. In order to realize clearly the nature of the molecular conceptions on which the Theory of Capillarity is based, let us imagine a homogeneous cube of a solid or liquid substance

(it is not at present necessary to distinguish), and with each surface subject to the same pressure.

If this pressure be increased, we know that the volume of the cube diminishes; and since the diminution is proportional to the volume, it follows that, if we have regarded the cube in the first instance as composed of an indefinitely large number of similar separate uniformly distributed molecules the sum of whose masses is the mass of the whole cube and whose masses are independent of their situation, we must now regard the intramolecular distances as uniformly diminished throughout the cube; and since a definite increase of pressure results in a definite contraction of volume after which the solid again reaches a condition of equilibrium, we may attribute to the molecules a repulsive force which increases as the intramolecular distance is diminished.

If, keeping the volume constant, we raise the temperature, the pressure exerted by the faces of the cube is increased, and we infer that the repulsive force between the molecules increases with the temperature of the body.

Since, again, a lowering of the temperature is attended by a uniform contraction of volume even when the external pressure is zero, we infer that the contraction is due to an intramolecular action equivalent to an attractive force, and that the expansion accompanying a rise of temperature is due to the repulsive action overbalancing this attractive force, and since the expansion of the substance results in the attainment of a condition of equilibrium in which the attractive and repulsive actions must be equal, we conclude that *the repulsive action diminishes more rapidly with an increase of molecular distance than does the attractive force*, and that, conversely, *the repulsive action increases with a diminution of distance more rapidly than the attractive.*

It may, however, be urged here that the facts mentioned thus far would be equally well accounted for on the supposition that the repulsive force increased with an increase in the distance between the molecules, but that the attractive force increased more rapidly. This, however, would require that the repulsive force should diminish as the temperature is raised, a supposition which it would be very difficult to reconcile with what we know of the nature of heat, and which we must therefore reject. Indeed it is important to remember that, in framing a statical theory of molecular equilibrium, our choice of alternative hypotheses may sometimes be guided by information which we possess as to the nature of the dynamical phenomena for which we are seeking an equivalent representation.

It will be observed, however, that, so far as we have gone, there is nothing to tell whether the attractive force increases, decreases, or is constant for a diminution of distance.

We are unable to separate with certainty the repulsive action we have spoken of into two parts, one of which might be due to the temperature and the other to what might be called an inherent elasticity of the molecule. The whole action was called by Poisson and writers before him " the repulsive force of heat "—a phrase which, because it is not entirely in harmony with the modern theory of molecular motion, has fallen into disuse.

Unfortunately the important relation between phenomena which it served to express has also been lost sight of. Whatever the repulsive and attractive forces and the intramolecular distances that we are speaking of may turn out to be, we may be quite sure that what used to be called the repulsive force of heat does in solids and liquids vary with alterations of molecular distances more rapidly than does the force of molecular attraction. It is on this fact, clearly pointed out both by Young and Poisson, that the whole theory of capillarity is based. I shall therefore not hesitate to use the phrase " repulsive force of heat " precisely as it was used by Poisson, to signify the whole of the repulsive action of which I have spoken. Those who recognize in the phenomena of molecular diffusion and heat-conduction evidence that the internal pressure not only in gases, but also in homogeneous solids and liquids, is really due to a transfer of molecular momentum taking place equally in opposite directions across any elementary area within the substance, will have no difficulty in perceiving that it is of this transfer of momentum that " the repulsive force of heat " is the statical equivalent, and that in assigning equal efficiency as a centre of force to each of the molecules we are really dealing with the matter statistically.

3. It is evident that but for the attractive forces between the molecules none of the phenomena of cohesion and adhesion could take place; and in the case of solids we are able to derive from observation of the breaking-stress some knowledge of the numerical value of the difference between the two forces.

We may, consistently with the phraseology we have used, regard a vertical solid bar of uniform section and subject to no atmospheric pressure as composed of horizontal layers of molecules, the distance apart of which layers is determined partly by the temperature of the bar and partly by the tension to which it is subjected. Let us fix our attention on the action across a plane horizontal section between the molecules at

each side of that section above and below it. If there is no tension, the position of equilibrium of the molecules is such that the attractive cohesion-forces and the repulsive force of heat across the section are equal. In my own mind the conception of what is going on is rendered more vivid by thinking of the analogy with two men who compress a spring placed between them by pulling each other together. The force with which they draw each other together is equal and opposite to the reaction of the spring by which they are thrust apart.

Now let the bar be stretched: the intramolecular distance is increased, and, by what we have seen, the repulsive forces are on this account diminished, while of the cohesion-forces we as yet only know that they must now be greater than the repulsive forces; and the equilibrium is now of a different kind: the resultant action across the section is now attractive; and since there is equilibrium, the molecules at either side of the section must be pulled apart by the action of molecules further away. The analogy which in my own mind gives vividness to the conception, is that of two men endeavouring by pulling at each other to compress a spring (now weaker than before) which is placed between them, while they themselves are somewhat pulled apart by others exerting less power than themselves. It is necessary for equilibrium that the cohesive force exerted across the section shall be equal to the sum of the tension and the repulsive heat-force; and the fact that we can increase the tension up to a certain value, the "breaking-stress," and not beyond, shows that after a certain point this condition ceases to he fulfilled.

If we write T for the tension per unit of area across the section, C for the cohesion per unit of area, and E for the repulsive action per unit of area, then $C = T + E$ or $T = C - E$ is an equation which holds for all values of T between O and the breaking-stress; but for an extension of the body greater than that corresponding to the breaking-strain, $C - E$ is less than the breaking-stress. In other words, with an increase of molecular distance the quantity $(C - E)$ increases up to a certain maximal value, beyond which an increase of the molecular distance is attended by a decrease in $(C - E)$.

Also we have seen that E diminishes with the extension; and that for extensions less than that corresponding to the breaking-strain its diminution is more rapid than that of C. Now it is evident that no maximal value could be attained by $(C - E)$ if C continually increased, remained constant, or continually diminished less rapidly than E; but that there would be a maximal value if C, after increasing, remaining

constant, or diminishing more slowly than E, were to begin to diminish more rapidly.

4. The significance of this result may be exhibited graphically with great advantage *.

Let O X and O Y be rectangular axes of coordinates, and along O X let distances be taken proportional to the distance between adjacent layers of molecules for different states of extension of the solid, and parallel to O Y let lines be drawn proportional to the attractive and repulsive forces in the interior of the liquid per unit area respectively at some given temperature. In this way we should obtain curves of attraction and of repulsion, the latter of which, from what we have seen, will slope downwards towards the axis of X; while the former may be represented by a curve such as that shown in fig. 1, which, after sloping less rapidly than the curve of repulsion, cuts that curve, and finally has the more rapid slope of the two. Let P be the point of intersection, P M the ordinate at P, and let N be the foot of the ordinate which cuts the curves where their tangents are parallel to one another.

If the intramolecular distance is less than O M, repulsion exceeds attraction, and equilibrium is only possible when there is an external pressure equal to the difference of the ordinates to the two curves. If the intramolecular distance O exceed O M, then equilibrium demands an external tension. At the extension indicated by O N this tension reaches its maximum value; and it is evident that the equilibrium is unstable, for beyond this distance a diminution of volume will mean an increase of attraction. The breaking-stress is therefore proportional to the difference of the ordinates at N. We shall afterwards return to this point when we come to consider the equilibrium of a liquid in contact with its vapour.

5. It is here only necessary to remark that the argument from the existence of the breaking-stress may be extended to liquids. For though we are prevented from determining the breaking-stress of a liquid in the same way as that of a solid by difficulties depending on the conditions of stability of liquid figures, yet there are many indications, derived partly from the adhesion to the top of a barometer-tube of a column of liquid more than barometric height, partly from the magnitude of the elastic resistance to compression, partly from the difficulty of starting ebullition in the interior of a liquid, and partly from capillary phenomena themselves, that the breaking-stress, if it could be determined, would in many cases be a

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* I owe to my friend Prof. Rücker the first suggestion of the graphical illustrations made use of in this paper.

quantity comparable with that of the metals themselves, while the extension corresponding to it would still be a very small fraction of the total volume of the liquid.

As regards the distance to which the attractive action of a molecule extends, it is customary to say that at all sensible distances the action is zero; and to regard the molecule as situated at the centre of an imaginary sphere whose radius is called the radius of molecular action, and whose surface marks the limit beyond which the cohesive attraction of the molecule is insensible, within which it is sensible.

It is to be observed, however, that inasmuch as a distance or an action which is insensible in one experiment may be sensible in another, the value of the radius of molecular action as defined in this way would probably vary with each experiment in which it is concerned. But we shall not require a more precise statement in the present investigation. Nor is it at present necessary to examine whether the number of molecules contained within the sphere of molecular action be great or small. The reasons which will afterwards appear for regarding this number as great rather than small are derived chiefly from capillary phenomena themselves.

Again, as regards the repulsive force, which is of the nature of an elastic reaction varying with the temperature, it is not at once apparent whether it is to be considered as exerted only between adjacent layers of molecules, or whether it extends to molecules separated from each other by intervening layers.

In the argument which follows we shall proceed upon the former supposition, the justification of which will be better understood after it is seen in what manner either hypothesis enters into the discussion.

6. In order to prove that the molecules of a liquid near the surface are in the condition which corresponds physically to a state of tension, let us select some non-volatile liquid, and imagine the molecules deprived of their attractive or cohesive action and of their repulsive action, and to be distributed at equal distances from each other, those at the surface lying in the same horizontal plane. Now let us endow each molecule with the attractive force which we ascribe to it in nature. Each molecule now exerts an attraction over those of its neighbours which fall within the radius of molecular action. We will suppose that the uniform distance which we have arbitrarily selected as that which shall separate adjacent molecules is small in comparison with the radius of molecular action, a condition which (for reasons that will afterwards be detailed) we believe to obtain in the mass of the liquid in nature. Let us select a molecule A at the surface, and

imagine that we describe about it as centre a sphere of radius equal to the radius of its molecular action. The molecules which exercise on this surface-molecule any attractive action are contained in the hemisphere at whose centre it is situated. From the symmetry of their distribution it is evident that their total resultant action is vertically downwards, also that the resultant action of each successive layer of molecules on the central one which we are considering is vertically downwards. We do not know the law according to which the attraction between two molecules varies with the distance. The only assumption we shall make is, that within the limits of variation with which we shall deal the attraction does not increase with the distance.

Let F_1 represent the vertical component due to the action of the first adjacent layer on the molecule A, F_2 that due to the second layer, F_3 that due to the third, and so on.

The last term to be considered is the nth or F_n, where n is the number of times that the distance between consecutive layers is contained in the radius of molecular action.

Now let us introduce between the molecules such repulsive forces as shall be consistent with the maintenance of equilibrium at the uniform distance apart which we have assigned, and let us proceed to examine what this repulsive force must be.

The total action downward on the surface-molecule A which we are considering is

$$F_1 + F_2 + F_3 + \ldots + F_n = \Sigma F.$$

If its equilibrium is to be maintained, it must experience a repulsive pressure upwards equal to ΣF, and every molecule in the surface-layer will be similarly acted on.

Also, since we cannot but suppose that to the action there is an equal and opposite reaction, the repulsive pressure on the first layer upwards is equal to that on the second layer downwards; and since the uniform distribution with which we have started implies that there are the same number of molecules in each layer, the repulsive pressure downwards on each molecule (B) of the second layer is equal to the upward pressure on each molecule A of the first.

Now let us consider the *attractive* actions on a molecule (B) of the second layer. These are ΣF downwards and F_1 upwards; and therefore, taking into account the repulsive pressure from above, the total resultant action downwards on (B) is

$$2\Sigma F - F_1 = F_1 + 2F_2 + 2F_3 + \ldots + 2F_n,$$

and to maintain equilibrium it is necessary that this should

be the repulsive reaction between (B) and the third layer; and this exceeds the repulsive reaction [(1) (2)] between A and the second layer by the amount

$$F_2 + F_3 + F_4 + \ldots + F_n.$$

Again, the total *attraction* downwards on every molecule C of the third layer is ΣF. The repulsive pressure downwards is $2\Sigma F - F_1$, and the upward attraction is $F_1 + F_2$. Therefore the total resultant action downwards is

$$3\Sigma F - 2F_1 - F_2 = F_1 + 2F_2 + 3F_3 + 3F_4 + \ldots + 3F_n;$$

and to maintain equilibrium this must therefore be the repulsive reaction [(3) (4)] between each molecule C and the fourth layer ; and this exceeds the repulsive reaction [(2) (3)] by the amount $F_3 + F_4 + \ldots + F_n$.

Similarly, the repulsive action [(4) (5)] between the fifth layer and a molecule of the fourth will exceed the reaction [(3) (4)] by the amount $F_4 + F_5 + \ldots + F_n$, and that between the $n + 1$th layer and a molecule of the nth will exceed that between the nth layer and a molecule of the $(n-1)$th by the amount F_n, after which the excess will be zero. It is thus seen that, in order to maintain the equilibrium, the repulsive reaction between consecutive layers must increase with the distance from the surface till a depth equal to the radius of the molecular action is attained, after which a constant value is required.

7. Now let us assign to the liquid such a temperature as shall maintain the molecules in the interior at the distance apart at which we have placed them.

The repulsive reaction is now too great to maintain the equilibrium of the molecules near the surface. If left to themselves, these molecules will recede from one another, and those at the surface will recede furthest. In other words, the density of the liquid will diminish as we rise to the surface; and it is evident that such a condition is one of stable equilibrium, and therefore permanent. For by the increase of distance the repulsive heat-force diminishes, as we have seen, more rapidly than the force of cohesive attraction.

We may either suppose the readjustment of the molecules near the surface to involve only an increase in distances parallel to the surface, while the distance between adjacent layers measured normally to the surface remains the same as in the interior of the liquid; or, on the other hand, the adjustment may involve an increase in molecular distances both parallel and perpendicular to the surface. The latter supposition is the more general, and, as we shall see later, is

the most easily reconciled with the phenomena of evaporation; and though either hypothesis will lead us to the same results, we shall find no reason for supposing that the pressure at any point near the surface of a liquid, whether within the liquid or in the vapour contiguous to it, is not equal in all directions, and shall therefore keep before us the latter of the two hypotheses; though the reader should bear in mind that in the conclusion we have now arrived at—that in a non-volatile liquid exposed to a vacuum there must be a diminution of density as the surface is approached from within— the other interpretation of the phrase " diminution of density " is possible. Now, if we desired to diminish the density of the interior of the mass of liquid, keeping its temperature all the time the same, so as to reduce its molecules to the same condition as at any given very small depth below the surface, we could do it by *stretching* the liquid. But to say that the condition of the molecules near the surface is that into which we should reduce the molecules of the interior by establishing among them a state of tension, is equivalent to saying that the surface-layers consist of liquid which differs from the liquid in the interior by being in what we call a state of tension; and it is evident that the tension increases as the surface is approached.

And it is further obvious that this tension will be exerted on any solid wall cutting the surface. For if we imagine a homogeneous cube of solid or liquid matter held in a state of isotropic tension by adhesion to solid walls, we perceive that the molecular condition which corresponds to equilibrium between the wall and the *stretched* mass is one of a tension on the wall. A solid wall, therefore, which cuts through the liquid surface so that part is above and part below the surface will only be in equilibrium with the layers near the surface when the portion in contact with them is in a state of tension; and the argument holds equally well if liquid wall be substituted for solid. (It is also to be observed that a plane solid surface laid horizontally upon the liquid surface will, if we adopt the more general supposition, also experience a tension at the first moment of contact.)

Two solid walls connected by a liquid surface will therefore be drawn together, and, if capable of motion, will absolutely move towards each other. Their motion involves the diminution of the liquid surface between them, which in turn requires that many molecules which have previously been so near the surface as to be separated by greater distances than those in the interior are now brought into the mass of the liquid, and their distance apart diminished. Now the exten-

sion of a solid or liquid substance by an external force involves
in general a fall of temperature ; the release from the state of
tension and consequent contraction involves a rise of tempe-
rature. Consequently the heat-energy necessary to endue the
less dense surface liquid with its given temperature is more
than sufficient to maintain this liquid at the same temperature
when its density is assimilated with that of the mass of the
liquid. The contraction of the surface is therefore accom-
panied by an evolution of heat-energy and a rise of tem-
perature; *and the surface-layers may be regarded as a portion
of the liquid on which extra heat-energy has been spent in sepa-
rating the molecules against the action of cohesive forces.*

8. We have, for the sake of clearness, first supposed the
liquid to be non-volatile, so that the surface should have above
it a vacuum entirely without action on the liquid below. We
will now proceed to the more general case of a liquid (α)
in contact with some second substance (β).

Let the surface of separation be a horizontal plane, and
let us think of (α) as the lower substance, and let us imagine
the second substance (β) to have its molecules uniformly dis-
tributed and rigidly connected so that a pressure or tension
is transmitted through it without producing any appreciable
change of density, while we examine what must be the condi-
tion of equilibrium of the liquid (α) in the neighbourhood
of the surface. We shall also suppose that the liquid (α) has
its molecules uniformly distributed at first, and they are en-
dowed with the cohesive attraction which they would possess
in nature. We will, as before, use F_1 to signify the resultant
vertical attraction between any molecule of (α) and the
adjacent layer; F_2, F_3, ... F_n for the corresponding action
between each molecule and more distant layers, and, as
before, we will write $F_1 + F_2 + F_3 + ... + F_n = \Sigma F$.

The action between (β) and (α) may be regarded as made
up of the action of each molecule of (α) on each layer of mole-
cules of (β), if we write ϕ_{A_1} for the action between any molecule
A of the surface-layer of (α) and the first layer of (β), ϕ_{A_2} for
the action between the same molecule and the next layer of
(β), and so on.

We may write $\Sigma \phi_A = \phi_{A_1} + \phi_{A_2} + \phi_{A_3} + ... + \phi_{A_m}$ for the
whole action of (β) on the molecule A.

Similarly, the action of any molecule B of the second layer
of (α) on the substance (β) will consist of a number of similar
terms of which an appropriate symbol for the first will be
ϕ_{B_2}, since it expresses the attraction between the molecule B
and the lowest layer of molecules in (β), which is the second
adjacent layer above it.

And we may write the whole action

$$\Sigma\phi_B = \phi_{B_2} + \phi_{B_3} + \phi_{B_4} + \ldots$$

Similarly,

$$\Sigma\phi_C = \phi_{C_3} + \phi_{C_4} + \ldots$$

expresses the action between the substance (β) and a molecule C of the third layer; and if there be, in the substance α, n^2 molecules per unit of area, the total action of (β) on (α) per unit of area may be written $n^2 \int \Sigma\phi$; and since the second substance (β) is in equilibrium with the uppermost layer of (α), this must be equal to the repulsive reaction downwards on each unit of area of the uppermost layer of (α). Therefore the pressure on this layer is $n^2 \int \Sigma\phi$ per unit of area, or $\int \Sigma\phi$ per molecule; and the total action on a molecule A of the first layer is therefore made up of $\int \Sigma\phi$ (downwards) $+ \Sigma F$ (downwards) $- \Sigma\phi_A$ (upward); and this must therefore be the value of the repulsive pressure between the second layer of the liquid (α) and every molecule A of the first layer; or, using previous notation,

$$[(1)(2)] = \int \Sigma\phi + \Sigma F - \Sigma\phi_A.$$

Again, the total action on every molecule (B) of the second layer of (α) will be

$$\left(\int \Sigma\phi + \Sigma F - \Sigma\phi_A\right) + \Sigma F - (F_1 + \Sigma\phi_B),$$

which is therefore the value of the elastic repulsive reaction between the third layer and the molecule B,—or

$$[(2)(3)] = \int \Sigma\phi + 2\Sigma F - \Sigma\phi_A - \Sigma\phi_B - F_1.$$

Similarly,

$$[(3)(4)] = \int \Sigma\phi + 3\Sigma F - \Sigma\phi_A - \Sigma\phi_B - \Sigma\phi_C - 2F_1 - F_2,$$

and

$$[(4)(5)] = \int \Sigma\phi + 4\Sigma F - \Sigma\phi_A - \Sigma\phi_B - \Sigma\phi_C - \Sigma\phi_D - 3F_1 - 2F_2 - F_3,$$

and

$$[(r)(r+1)] = \int \Sigma\phi + r\Sigma F - \Sigma\phi_A - \Sigma\phi_B - \ldots \Sigma\phi_r - (r-1)F_1 - (r-2)F_2 \ldots - F_{r-1};$$

from which we find

$$[(2)(3)] - [(1)(2)] = \Sigma F - \Sigma\phi_B - F_1$$
$$= F_2 + F_3 + F_4 + \ldots - (\phi_{B_2} + \phi_{B_3} + \phi_{B_4} + \ldots)$$
$$[(3)(4)] - [(2)(3)] = \Sigma F - \Sigma\phi_C - F_1 - F_2$$
$$= F_3 + F_4 + \ldots - (\phi_{C_3} + \phi_{C_4} + \phi_{C_5} + \ldots);$$

2 A 2

and for the repulsive reaction between the $(r+1)$th layer and a molecule R of the rth layer, we have

$$[(r)(r+1)] = F_r + F_{r+1} + \ldots - (\phi_{R_r} + \phi_{R_{r+1}} + \ldots)^*.$$

Now if $\Sigma F > \Sigma \phi_A$, *i. e.* if the action of the liquid (α) itself on a surface-molecule is greater than that of the substance beyond the surface, we may assume $F_1 > \phi_{A_1}$, $F_2 > \phi_{A_2}$, and so on. For this will be the case if the condition $\Sigma F > \Sigma \phi_A$ is due, on the one hand, to a less density of the molecular structure of the substance (β), or, on the other hand, to a smaller intrinsic energy in the molecules of (β); or, thirdly, to both of these causes combined; and it is difficult to conceive of any other cause than one of these.

In this case the value of each of the expressions

$$[(2)(3)] - [(1)(2)], \quad [(3)(4)] - [(2)(3)], \text{ \&c.}$$

is positive; and equilibrium at a given temperature can only be obtained by an increase of repulsive reaction (*i. e.* of density) as we descend into the substance.

If, again, $\Sigma F = \Sigma \phi_A$ in such a manner that

$$F_1 = \phi_{A_1}, \quad F_2 = \phi_{A_2} = \phi_{B_2}, \text{ \&c.,}$$

then it is evident that we have at the opposite sides of the surface two substances in which the physical properties with which we are concerned are identical, and the value of each of the expressions $[(2)(3)] - [(1)(2)]$ &c. becomes zero, and the density at each side of the surface is everywhere the same, and there is no surface-tension.

If, on the other hand, $\Sigma F < \Sigma \phi_A$, the substance (β) must have, owing either to greater density or to greater intrinsic energy of its molecules, a greater action on a surface-molecule of A than the liquid itself, and we may assume that any term F_n is greater than the corresponding term ϕ_{A_n}, or ϕ_{B_n}, or ϕ_{C_n}, &c. Therefore the value of each of the terms

$$[(2)(3)] - [(1)(2)], \quad [(3)(4)] - [(2)(3)], \text{ \&c.}$$

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* The meaning of this result may with advantage be illustrated by the geometrical diagram (fig. 2), which will not require explanation. The downward attraction on the elementary volume A may be written $\Sigma_F^F \underset{r}{n} F$; the upward attraction $\Sigma_\phi^\phi \underset{r}{n} \phi$. If there is to be equilibrium, the difference of these two must be balanced by the difference in the repulsive pressure on the upper and lower surfaces of the elementary volume.

If (β) is exchanged for a vacuum, $\Sigma_\phi^\phi \underset{r}{n} \phi = 0$, which gives the result of the first case.

will be —ve, and equilibrium can only be attained by a decrease of density in the liquid (α) as we pass inwards from the surface. In this case therefore the liquid (α) will be condensed upon the surface of the substance (β); and its surface-layers will exhibit, instead of a tension, a pressure, and the surface of contact will tend to enlarge itself, the liquid in the neighbourhood of the surface possessing, per unit of volume, less energy than the liquid in the interior.

9. Now that we know how a liquid of uniform density, to start with, would behave if placed in contact with a uniform substance, we can tell how two different liquids, each supposed uniform to start with, will behave when placed in contact with each other. There will be a readjustment of each near the surface in the direction either of an extension or a compression according as what may, for brevity, be called the mutual attraction of the liquids is less or greater than what we may call the self-attraction. We shall return to this result after examining the equilibrium at the surface of a gas or vapour.

It is necessary, before we can decide how far our results apply also to vapours and gases, to extend to their case the same statical treatment which we have used with liquids.

10. When the temperature and pressure of a gas are such that it is far removed from its point of liquefaction, we find no trace of any attraction between the molecules, but only of repulsion ; and we may regard the phenomena of gases from a statical point of view by considering the molecules to be beyond the radius of each other's molecular attraction, but not beyond that of molecular repulsion, which latter force now varies inversely as the volume, and therefore inversely as the cube of the molecular distances.

That we know, in the case of gases, something of the dynamical conditions which produce what we are calling the repulsive force, need not prevent us from adopting the statical point of view, which may also be regarded as statistical.

If the temperature be below what is called the critical temperature of the gas, we can, by sufficiently increasing the pressure, liquefy it, and the liquid will only exist as such so long as the pressure above it is maintained. In fact, the interior of a liquid in equilibrium with its own vapour is in a state of compression. There is, however, nothing in this that is inconsistent with the rarefaction of the surface-layers, as may be seen from the following considerations.

For we may imagine that upon the surface of a non-volatile liquid exposed to a vacuum one or more additional layers of molecules are laid, which molecules will be attracted downwards by an excess of cohesive force, and will therefore exert

a pressure on the layers immediately below; but the downward action is accompanied by an equal and opposite upward attraction exerted by the new molecules on those below, so that no additional pressure (other than that due to gravitation) will be transmitted to a sensible depth, and the only effect will be to shift upwards the condition of surface-extension. What were previously the first, second, third layers, &c., are now each at a greater depth below the surface, and the molecular distances are in each case diminished, but are still greater than in the interior of the liquid, unless the number of new layers added be so great that the original surface lies now at a sensible depth within the liquid. Then, and not till then, the condition of rarefaction will disappear. Now the mechanical pressure, such as that which we may conceive to be produced by the impacts of a gas above the liquid surface, differs from the pressure we have described in not being attended by an equal upward attractive action, and consequently its pressure will be transmitted to the whole liquid mass below, but the amount of diminution which it produces in the rarefaction at any point near the surface will be less than that produced in the way described, if the mechanical gaseous pressure is less than the increase in cohesive action at that point due to the addition of the new layers.

Now our knowledge of the value of the surface-tension, and of the smallness of the depth to which it extends, obliges us to conclude that the extension to which, as we have seen, it is due is such as must be attended by a diminution of cohesive action so considerable as to be far greater than any gaseous pressure to which liquids are exposed in our experiments on surface-tension. Consequently the rarefaction of the surface-layers, even in a direction normal to the surface, will be diminished by such pressure, but by no means destroyed. Thus we shall have the pressure of a gas above transmitted through rarefied layers to the liquid below, just as, conversely, a solid wall may condense a rare liquid at its surface, and yet a mechanical tension may be transmitted through the wall and condensed layers to the liquid beyond.

Let us now examine what would happen if the outermost molecules of a liquid, with a vacuum above its plane surface, were at such a distance from the next layer that the least oscillation outward would carry them beyond the range of molecular attraction of the rest of the liquid. The position is one of unstable equilibrium with respect to such oscillations, and the molecules, unless absolutely stationary, will escape into the space beyond, where they will, considered from a statical point of view, exert only a repulsive force, will arrange

themselves at uniform distances apart, and will exercise a pressure on the surface-molecules of the liquid, which, by causing them to approach the interior molecules more closely, will render their position one of stability for indefinitely small oscillations. For more considerable oscillations, however, the position of the remaining surface-molecules will still be one of instability : hence, if the molecules are subject to such oscillations, still more will evaporate, and the pressure of the vapour above the liquid will increase, and this will go on till an equilibrium is attained, as it evidently ultimately will be, both on account of the increase of pressure and of density in the vapour.

Let us now suppose the volume to be diminished, so that the pressure is increased. The molecules of the vapour can readjust themselves to such increased pressure, so also can those of the liquid ; and the new equilibrium of liquid and vapour under increased pressure will obviously be stable, *provided that the molecules of the gas are not in their turn subject to oscillations.* If, however, a molecule of the gas be carried to a position nearer the liquid than that to which a liquid molecule may oscillate and yet be in equilibrium, it will evidently not return, and there will be a condensation of vapour into liquid. Hence, by admitting that the gaseous molecules also are liable to sufficiently great oscillations, we see that a reduction of pressure to the original amount will take place. If the reduction goes beyond this the rarefaction of the surface-layers will increase, so that a smaller oscillation of a liquid molecule will suffice to secure its escape, which points to a condition of stable equilibrium. It may be remarked also that the pressure of a different gas above the liquid will, by its pressure, increase the stability of the surface-molecules, and thus retard evaporation.

·11. If we now return to the graphical representation of attractive and repulsive forces, which we have seen reason to believe to hold good for liquids as well as for solids, we find that at the extension corresponding to the breaking-strain the attraction-curve is above the repulsion-curve, and begins to slope more rapidly. Hence, if this condition continues, the curves must again cut one another, and the repulsion-curve be uppermost. In other words, a state will ensue in which repulsion exceeds attraction. Now this is what we find in a gas, but, further, in a perfect gas repulsion diminishes with an increase of volume, a condition which can only be represented by the repulsion-curve sloping more rapidly than the attraction-curve. Hence, if the gaseous and liquid states are continuous, there must be some distance, such as OQ (fig. 3),

at which the two curves are again parallel. Now it is very interesting to remark that for any extension between those indicated by N and Q the equilibrium is unstable; for between N and the ordinate to the second intersection a diminution of volume is attended by an increase of attraction, while between the ordinate to the intersection and Q an increase of volume is attended by an increase of repulsion. The first corresponds to the oscillation of liquid molecules outwards, the second to the oscillation of gaseous molecules towards the liquid.

Hence we see that, when a liquid is in contact with its vapour, there is a limit, on the one hand, to the rarefaction possible for the former at the surface, and, on the other hand, to the condensation possible to the latter—a result which explains the sudden transition from the density of the liquid to that of the vapour. Within these limits the rarefaction and condensation will evidently still take place; for the conditions of the investigations which we gave for the contact of two liquids are, so far as the denser liquid is concerned, unaltered, except by the presence of a mechanical pressure, which, as we have seen, will not affect the character of the result; while the vapour which is substituted for the less dense liquid of the investigation fulfils the one essential condition that the pressure-curve shall slope more rapidly than the attraction-curve—the fact that it, too, is in a state of pressure not affecting the result. If the dilatation near the surface of the liquid only took place parallel to, and not also normally to, the surface, the equilibrium of the liquid molecules for outward oscillations would be much more stable; but we know that when a liquid is passed up into a barometric vacuum the evaporation is extremely rapid, a fact which indicates that the surface-layers are very near the limit of stability with respect to outward oscillations, and which confirms the supposition that the dilatation takes place in all directions.

We are thus led to the conclusion that a solid wall cutting the surface-layers of a liquid transversely will experience a pressure due to the vapour and a tension due to the liquid near the surface, the resultant action being the difference between the two.

12. Since a solid whose surface is exposed to a gas does not exhibit the phenomenon of a surface-tension—for its edges and angles are not rounded as they would be were the surface-tension efficient in modifying the figure of the solid— we must conclude that the internal friction among its molecules permits a state of strain to exist between the surface-molecules and those in the interior. Thus if we were suddenly to expose the interior of a mass of water to the air,

the molecules of the liquid near the newly exposed surface would at once readjust themselves to the new conditions of equilibrium, receding from each other and absorbing heat. But if we did the same to a solid, it is very probable that the readjustment of the intramolecular distances would not take place. The experimental evidence that at the surface of solids there exists a layer of condensed gas is very strong; and just as a gas may be liquefied by an external pressure, so it is possible that the molecular pressure caused by the attraction of the solid may condense on its surface in a liquid form some or all of the gases contained in the atmosphere to which it is exposed. It is to be expected that the gases of our atmosphere which are most readily liquefied by pressure, viz. water-vapour and carbon dioxide, are those which will be most condensed at the surface of solids exposed to it; and in experiments in which the liberation of the condensed gases is effected, it is these which may be expected to appear in greatest quantity. With respect, however, to those gases whose critical temperature is below that at which capillary experiments are usually made, it is to be observed that, although they will be condensed at the surface of a solid, yet the outer surface of the condensed stratum will not exhibit the phenomena of a surface-tension. For the experiments of Andrews and Ramsay, which are confirmed by Cailletet and Jamin, show that above the critical temperature the densities of the gas and the liquid are identical. Hence in the case of such a gas there will be a continuous though very rapid diminution of density in the condensed stratum as we pass outwards from the solid surface into the unmodified gas beyond. Nowhere can the condensed film be in a state of tension, for we have seen that the state which we call the surface-tension is due to the molecules being in the condition to which we could reduce the molecules of the interior of the liquid by stretching. But a liquid which is only kept liquid by pressure above its critical temperature cannot sustain a tension. For let us imagine a portion of such a liquid enclosed within solid walls, and then removed for experiment, and let the experiment consist in mechanically enlarging the space enclosed by the walls. The liquid will expand, and will pass without breach of continuity into a gas which will continue to expand, but will continually exert a pressure, and never a tension, on the enclosing walls. For this statement of the continuity of liquid and gaseous conditions above the critical temperature we have experimental evidence.

13. Now it is interesting to observe that our diagram of

the repulsion- and attraction-curves leads us to anticipate this condition of things; for we know that an increase of temperature, when the volume is kept constant, involves an increase of pressure, which implies that the ordinates to the repulsion-curve must be everywhere increased, but most to the left-hand end of the curve, since the increase of pressure when the volume is kept constant is far greater in a solid or liquid than in a gas; thus an elevation of temperature implies a bodily shifting of the whole curve upwards with an increase in the slope as we approach the left-hand end.   Now the shifting alone would lift the curve quite above the curve of attractions (see fig. 4), which would mean that above a certain temperature repulsion would always exceed attraction, or that the substance could only exist under pressure.   There would still, however, be the same region of instability as before, and consequently the surface of discontinuity between liquid and vapour would still exist; but by a sufficient increase in the slope of the repulsion-curve, such as we have seen will also take place, this region of instability will diminish and finally disappear (see fig. 5) when the slope of the repulsion-curve is everywhere greater than that of the corresponding part of the attraction-curve. At the temperature at which this takes place all discontinuity will disappear, and the substance will be in the same condition throughout.   Up to this point the liquid will still exhibit within the vessel in which it is contained the *phenomena* of a surface-tension, though in reality the wall of the containing vessel will experience, after the temperature has been reached at which the repulsion-curve ceases to cut the attraction-curve, only a pressure even where it cuts the liquid surface.   But the pressure will be less here than elsewhere, for our original investigation always holds within the limits for which the slope of the repulsion-curve is greater than that of the curve of attractions.   Thus it is probable that the meniscus observed at the surface of liquefied oxygen or nitrogen does not correspond to a *true* tension as in the case of water or mercury.

14. If our method of dealing with the continuity of the liquid and gaseous states be compared with that of Professor James Thomson (as quoted on pages 124–126 of Maxwell's 'Theory of Heat'), it will be seen that the ordinates to the isothermal curves there given correspond to the difference of the ordinates to the two curves in the above investigation—that, in fact, the horizontal axis of coordinates in Maxwell's diagram (which is reproduced in fig. 6) represents our attraction-curve.   The suggestion which Professor Thomson made thirteen years ago—that the portion A B C of the curve, which we know from experimental evidence to represent the conditions

of the liquid, and the portion G H K, which we know to represent conditions of the vapour, are not really discontinuous, but are joined by a portion C D E F G, of which the part between D and F must be unstable—is very similar to our own argument from the two curves.

The advance that we have been able to make on Professor Thomson's suggestions is, that we have shown that it is a necessity of the equilibrium of the liquid that near the surface it shall be less dense than is indicated by the point C, *i. e.* that the curve does pass below this point. Further, that, in the case of liquids whose vapour-pressure at the given temperature is not enormously great, there is near the surface a region of true tension—that is, that the curve passes *below the horizontal axis of coordinates* in Maxwell's diagram; while by the argument from the breaking-strain we see that, after a certain volume has been reached, the corresponding tension diminishes, *i. e.* we have experimental evidence of the existence of the curve down to and even beyond the turning-point D. Again, by showing that it is a necessity of equilibrium that the vapour should be condensed at the surface of the liquid, we have been able to prove that the vapour really exists there in the condition indicated by the curve between G and F.

Thus Professor Thomson's suggestion (see Maxwell's 'Heat,' p. 127) that such a state of things as is indicated by his hypothetical part of the curve "may exist in some part of the thin superficial stratum of transition from a liquid into its own gas, in which the phenomena of capillarity take place," is shown, by our method of considering the question, to have been a correct anticipation.

We may now observe, with respect to the hypothesis which we have used throughout, viz. that the repulsive force is only exerted between contiguous layers of molecules and not between more distant layers, that this conception of the force is the only one by which we can represent statically the phenomena of impact by which we believe the repulsive action to be really due. The choice of this hypothesis is, in fact, one of those to which we are guided by our knowledge of the dynamical phenomena ; and this fact itself, and the completeness with which the hypothesis serves to express the phenomena, points to the correctness of the choice, which could be further justified by showing that any more general hypothesis would not express the phenomena without the introduction of complicated restrictions.

15. The next step which it is necessary to take is to show that the investigation we have given would be in no way affected if the surface of the liquid were curved instead of

plane, provided that at every point the least radius of curvature is very great in comparison with the radius of molecular action.

Let a sphere whose radius is the radius of molecular action be described about any ....¹e A at the surface of a liquid, and let the figure (fig. 7) represent a section of the curved surface containing the normal to the point A and the least circle of curvature, and let B and C be the intersections of the surface with the sphere; PAQ the section of the plane tangent at A whose intersections with the sphere are P and Q. Then, if the radius AP is very small in comparison with the least radius of curvature, the portion of the curve BAC is not to be distinguished from the least circle of curvature, and BP or CQ is very small in comparison with AP; and if a similar normal section through A were made in any other plane for which the radius of curvature was greater, the points corresponding to B and C would be still nearer to the tangent-plane. Also, if a smaller sphere were described about the molecule A whose intersections in the plane of the paper with the curved surface were b and c and with the tangent-plane p and q respectively, then the ratio of the distance bp to the radius Ap would be less than the ratio of BP to AP, and the same would be true for any other normal section through A.

Now, in the investigation we have given, the terms F_1, F_2, F_3, &c., have represented the action, on a given molecule, of successive horizontal layers of molecules; and it is evident that if each layer, instead of being flat, were bent so as to be parallel to the slightly curved surface, the difference in the action of each molecule of the layer, and therefore of the whole layer on the given molecule, would be negligible in comparison with the whole action of the layer.

Again, the tension at any small depth below the surface has been shown to be due to the variation, from the value in the interior, of the repulsive action which it is necessary to establish at that depth among evenly distributed molecules if equilibrium is to be maintained, and the readjustment of the molecular distances by which the equilibrium is secured in nature has, as we have seen, the effect of diminishing the repulsive action still further, and of thus increasing the difference between its value at the given depth and the value in the interior.

Now the difference between the repulsive action of the first and second layers was seen to be

$$F_2 + F_3 + F_4 + \ldots \ldots ;$$

for an even distribution of molecules, and after self-adjustment it will be still greater. Similarly, the difference between the repulsive action of the second and third and that of the first and second layers will be greater than

$$F_3 + F_4 + \ldots,$$

and so on.

Therefore the difference between the repulsive action in the interior and that between the first and second layers is greater than

$$F_2 + 2F_3 + 3F_4 + \ldots$$

Similarly the difference between the repulsive action in the interior and that between the second and third layers is greater than

$$F_3 + 2F_4 + 3F_5 + \ldots,$$

and so on for greater depths.

And we have seen that no term of any of these expressions has its value sensibly altered by the curvature of the layers, and consequently the value of the tension at any depth will not be sensibly altered by the curvature, and the same reasoning is obviously applicable to the more general case of the surface of contact of any two fluids *.

16. We are thus led to the general conclusion that the layers of a fluid near and parallel to its bounding surface are, if the latter has a continuous and finite curvature, each mechanically equivalent to a perfectly flexible membrane, the tension or pressure on which is equal in all directions and at every point, and depends for its value on the nature of the substances at the two sides of the surface. When two fluids are separated by a common surface of contact, the surface-tension, which is the subject of observation and measurement in physical experiments, is the algebraic sum of all the tensions or pressures at the two sides of the surface acting on an area of insensible depth in either fluid.

17. If we call one fluid A and the other B, then, if the mutual attraction between A and B is greater than what we have called the self-attraction of A, and also is greater than

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* It is to be observed that to obtain this result we have tacitly made use, for the first time, of the assumption that the number of molecules within the sphere of molecular attraction is great; for otherwise a slight curvature of the layers might cause an important alteration in the number of molecules, and therefore in the mass of matter constituting the effective portion of each layer; and the justification of the assumption is to be found in the fact that all the phenomena of capillarity show the surface-tension to be independent of the curvature of the surface so long as the least radius of curvature is of sensible and measurable magnitude.

the self-attraction of B, then each fluid will be condensed at the common surface, which will therefore be in a state of pressure. Now, as Maxwell has pointed out[*], when this is the case the surface must be unstable, for its extension involves an evolution of energy being aided by the molecular forces, and the surface will therefore tend to enlarge itself by puckering and replication. It is also probable that this condition would involve what we call chemical action. If, on the other hand, the mutual attraction between A and B is less than the self-attraction of A, and also is less than the self-attraction of B, then each fluid will be in a state of tension near the bounding-surface, which will therefore be in stable equilibrium, and the experimental surface-tension will be the sum of the two sets of forces.

There remains the case in which one fluid is condensed and the other rarefied at the surface. Here the two sets of forces are of opposite sign, and the surface will be stable or unstable according as the algebraic sum corresponds to a tension or to a pressure. A liquid in contact with its own vapour is, as we have seen, an instance of the former case [†].

18. When, on the other hand, only one of the substances is a fluid, the other being a solid, it is only the tension or pressure of the former that can produce any motion or that enters into experimental determinations; for forces normal to the solid are balanced by the resistance of the solid, and forces within the solid tangential to the surface cannot, owing to the rigidity of the solid, cause a motion of its parts.

Now in the case of the surface of contact of air and dense solids, such as glass or a metal, there can be no doubt, as we have seen, that the air is condensed on the solid, and that the surface-force within this fluid is a pressure, and from this we are forced to conclude that whenever the liquid-angle of contact between a liquid and a solid in air is acute (or 0°), the liquid also is condensed against the solid, and that, of the three surface-forces concerned, the greatest is the surface-pressure within the liquid in the neighbourhood of the solid, as is evident from a glance at fig. 8, which represents a section normal to the surfaces in question in the neighbourhood of the common line of contact O. And it will be perceived that the spread of a liquid over a solid, as for instance of a drop of alcohol over glass, is not quite the same pheno-

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[*] *Encyclopædia Britannica*, art. " Capillarity."

[†] The latter case, perhaps, corresponds to liquids which mix without chemical action ; for although, as Maxwell remarks, no case of puckering has been observed, yet it is not evident that the phenomenon is one which could be observed or distinguished from diffusion.

menon as the spread of one liquid over another, for example of a drop of alcohol over mercury; for in the latter case the spreading is aided by the tension-forces within the mercury, which cause a motion of its superficial parts, while in the solid these forces are, as we have seen, rendered inoperative by the internal friction. Moreover, we cannot decide in the same way whether the observed value of the tension at the common surface of the two liquids is a sum or a difference. In the case of the solid it is evident that the liquid cannot wet it unless it is condensed at the surface of the solid, *i. e.* unless the attraction of the solid for the liquid is stronger than that of the liquid for itself. If, besides, the mutual attraction of liquid and solid is stronger than the self-attraction of the solid, then the surface would be unstable but for the rigidity of the solid. If this rigidity gradually gave way, the surface of contact would extend, and the solid would mix with the liquid.

We thus obtain an explanation of the fact that a liquid which dissolves or acts chemically on a solid always "wets" it, and are led to a view of the nature of the *beginning* of solution much resembling that put forward by Mr. W. W. J. Nicol (Phil. Mag. Feb. 1883).

When, on the other hand, the liquid-angle of contact with the solid is obtuse, as for instance with mercury and glass in air, it is not possible to decide in the same way whether the surface-force within the liquid in the neighbourhood of the solid is a tension or a pressure. If it is a pressure, then it follows that the surface-pressure of air on glass is even greater than the experimental surface-tension of mercury, which, of substances that are liquid at ordinary temperatures, exhibits the greatest of all the surface forces that have yet been measured. This result would seem to find some independent confirmation in the fact that glass is hygroscopic, and slightly soluble in water, which is generally present in the air in which the contact-angle is observed. Experiments on perfectly dry surfaces—such, for instance, as those of Quincke with freshly split laminæ of talc before they have had time to condense aqueous vapour upon themselves—throw some light on this point, the further discussion of which is, however, beyond the object of the present paper.

19. I have aimed in this paper at proving directly, from consideration of the elastic and thermal properties of solids, liquids, and gases, the *reality* of the surface-tensions and pressure, since, from the principle of the surface-tension, if once admitted, when used in combination with the experimental fact of hydrostatics, that in a liquid acted on by gravity

alone the pressure or tension at any point is proportional to the depth below or above the free horizontal surface[*], all the phenomena of capillarity, the constancy of the contact angle, the horizontal motion of floating bodies, the equation to the liquid surface, and the laws which regulate the stability of liquid figures, may be easily deduced.

It has not been necessary to assume with Maxwell[†] that the contraction of a liquid surface takes place in conformity with the principle of the conservation of energy, and to deduce the surface-tension from a combination of this assumption with the molecular hypothesis. On the contrary, the fact that the contraction or extension of the surface which takes place is consistent with the principle of conservation of energy has flowed from the investigation itself; and this, I think, is a considerable advantage, for the assumption of the conservation of energy, on which Maxwell bases his own investigation, does not carry with it in molecular matters the security of previous experimental justification: it appears as an additional hypothesis used in conjunction with the other hypotheses as to the nature of the molecular actions, but it is one whose exact relation to the other hypotheses is not easily perceived, since it is partly implied in them already, and it

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[*] An insight into the nature of the hydrostatic pressure, due to gravitation at the earth's surface, and its connexion with the internal repulsive force of which we have spoken, is, I think, best obtained by the light of such a theory as that of Lesage, which attributes the gravitative action to the momentum of "ultra-mundane corpuscles."

On such a theory we may regard any horizontal layer of molecules as receiving a momentum from above, which would, in the absence of the earth, be met by an equal corpuscular momentum from below; but, owing to the earth's screening action, this compensating momentum is wanting, and must be replaced by an increase in the molecular momentum, which in the statical theory is represented by the repulsive force, and which is obtained by a diminution of the distance between the layer under consideration and that next below it, to which the effect of the corpuscular momentum is thus transmitted; this next layer thus receives from above, in addition to the corpuscular momentum proper to itself, a repulsive pressure equivalent to that belonging to the former layer; and the sum of these must now again be balanced by an increase in molecular pressure from the layer below, and so on throughout the liquid: thus there is an increase of density and of molecular momentum, *i. e.* of internal repulsion, as we descend. But the increase of molecular momentum which is thus substituted for the directed corpuscular momentum from below, cannot, from the nature of the motion in fluids, be supplied in one direction only, and is therefore recognized as what we call the hydrostatic pressure equally in all directions. It is thus seen that the hydrostatic pressure at any point due to the weight of the liquid is the excess of the repulsive force above the value which it would possess if the liquid were removed from the influence of attracting bodies.

[†] Vide article on Capillarity, *Encyc. Britannica* (present edition).

results that the argument carries less conviction than it would do if the relation between its hypotheses were more easily apprehended.

20. It is often a matter of interest to examine in what relation one method of investigating a physical problem stands to another ; and I shall endeavour in what follows to make clear why the incorrect assumption of Laplace, that the density of the liquid is uniform, leads, from his method of considering the question, to the same equation to the surface of a liquid as is obtained by Poisson, who takes the variation of density into account.

If we examine, as did Laplace, the difference of the action on the upper portion of an elementary filament of unit section, normal to a liquid surface at O when the surface is curved, as along AOB (fig. 9), from the action when the liquid is bounded by the tangent-plane COD (which we will for convenience suppose horizontal), we see that the difference is due to the excess or defect of liquid above or below the level of CD ; and the total differential action is due to the sum of actions between all elements such as M of the canal and each of the elementary volumes such as EF, into which we may suppose the differential matter divided.

Let us imagine it to be divided in the following manner :—

Let the sphere whose radius is the radius r of molecular action be described about the element M, and let spheres of radius $r-dr$, $r-2dr$, &c. be also described about the same point, so as to divide the differential matter under consideration into spherical shells of equal elementary thickness dr. Again, imagine that there pass through OP a series of vertical planes, the inclination of each of which to the next is the infinitesimal angle $d\theta$. The differential liquid comprised between any two consecutive spherical surfaces is now partitioned off into infinitesimal solid elements ; and if we confine our attention to all the elements contained between a single pair of spherical surfaces, we see that the dimensions of each in the direction of the radius of the spheres is the same, viz. dr, and in the horizontal direction at right angles to this radius is the same, viz. $Og \times d\theta$; but in the remaining direction EF, perpendicular to the other two, the dimensions of each element are not the same, but will depend in each case on the curvature of the surface. Now, provided that the curvature of the surface is always such that the radius of molecular action is insensible in comparison with the least radius of curvature, it follows that that portion of any normal section of the surface made through the point O, which falls within the sphere of molecular action described about any

point M of the normal filament OP, cannot be distinguished from the circle of curvature of the section in question.

But if the radius of molecular action be insensible in comparison with the least radius of curvature of the liquid at the point O, then the length EG will be insensible in comparison with the radius M*g*, and the action of the element E*g* on the element M may be regarded as taking place along any line joining M to any point of EF; *and this will be the case whether the density of the liquid be constant throughout* EF *or whether it vary*, provided only that the variation is insensible for depths which are themselves insensible in comparison with the radius of molecular action.

Now, if the radius of curvature of the section containing the element EF were different, viz. r' (but still so great that the radius of molecular action is insensible in comparison with it), so that length EF of the element in question were to become EF′, then, since the change of curvature evidently produces no change in any other dimension of the element, the ratio EF to EF′ is the ratio in which the volume of the element is altered, and it is easily shown, from the geometry of the circle, that

$$\mathrm{EF} : \mathrm{EF}' : : \frac{1}{r} : \frac{1}{r'},$$

and the same is true for the corresponding element in the section at right angles to the plane containing the line OP and the element EF, or, using a corresponding notation,

$$\mathrm{E}\phi : \mathrm{E}\phi' : : \frac{1}{\rho} : \frac{1}{\rho'} ;$$

whence, adding these two ratios,

$$\mathrm{EF} + \mathrm{E}\phi : \mathrm{EF}' + \mathrm{E}\phi' : : \frac{1}{r} + \frac{1}{\rho} : \frac{1}{r'} + \frac{1}{\rho'}.$$

Hence, if we consider the attractions as proportional to the volumes, we get that the attractions of *any pair* of corresponding elements of the differential liquid, in planes containing the filament OP and at right angles to each other, is proportional to the sum of the reciprocals of the radii of the circles of curvature in those two planes.

Now the sum of the reciprocals of the radii of the circles of curvature at any point in any two planes at right angles to each other is, by geometry, always equal to the sum of the reciprocals of the principal radii of curvature, $= \frac{1}{\mathrm{R}} + \frac{1}{\mathrm{R}'}$; and consequently the total integral action of the differential liquid above or below the plane surface, being made up of pairs of

terms each of which pairs is proportional to the quantity $\left(\dfrac{1}{R} + \dfrac{1}{R'}\right)$, is itself proportional to this quantity ; and this integral action is what is called the normal pressure or tension at the point O, due to the curvature of the surface ; and by equating the expression thus obtained to the hydrostatic pressure or tension at the same point expressed as a function of the distance of the point from the level of the free horizontal surface, we obtain the well-known equation to the liquid surface.

It is to be observed that that part of our own investigation in which we showed that the effect of the curvature on the surface-tension was insensible, is equivalent to proving that the action of the differential matter of the present instance *parallel to the surface* is insensible in comparison with the total tangential action. The existence of the effect normal to the surface is, in our own investigation, a consequence of the inclination between consecutive elements of the surface.

To ignore, as Laplace does, the variation of density near the surface is equivalent, as we can now see, to supposing the liquid to be inextensible and incompressible, or rather to supposing that the extension or compression near the surface, which we have found to be a necessity of the molecular equilibrium, is insensibly small.

Now, in our own investigation, it has not been necessary to inquire into the absolute value of the compression or extension at any point; such value must depend upon the coefficients of compressibility and of expansion with heat, and will be small when these are small ; and we may imagine our investigation to be made in precisely the same manner with a liquid for which both of these coefficients are insensibly small in all experiments. For such a liquid the uniform distribution of molecules, with which it was our method to start, must be only insensibly altered, *but must still be altered* near the surface to secure equilibrium, and a state of tension or of pressure will still be produced ; and we may still regard the free surface of such a liquid as a portion in which heat-energy has been spent in doing work against molecular attractions, though, since one factor of the work (viz. the increase of molecular distance) has now become an exceedingly small quantity, the other factor (viz. the molecular attraction) must now be correspondingly large if the surface-energy is to remain a quantity of the same order as before.

But if all liquids were like this which we are imagining, we should not have been able to make the experimental observations on expansion with heat and on compressibility necessary

to establish the relation between the force of molecular attraction and "the repulsive force of heat," on which our whole argument has been based. This relation is, as we have seen, the expression of a relation between observed quantities, and is one which we must suppose to hold good even in the limit where the observed quantities are vanishingly small. Laplace, by confining his attention to this limiting case, overlooked the relation, and accordingly failed to perceive the reality of the surface-tension; and his theory is in consequence absolutely inapplicable to the explanation of any of those phenomena of horizontal motion on a liquid surface which are due solely to variations of the surface-tension, and are not necessarily accompanied by an elevation or depression of the liquid.

XXXVIII. *The Nature of Solution.*—Part II. *Boiling-Points of Salt-Solutions. By* W. W. J. NICOL, *M.A., B.Sc., F.R.S.E., F.C.S., &c., Lecturer on Chemistry, Mason College, Birmingham*[*].

VERY little indeed is known of the temperatures at which salt-solutions of definite composition boil. Almost the whole of our knowledge is confined to the boiling-points of saturated solutions; and these have been determined in very many cases with but little pretence to accuracy. With the exception of the experiments made by Legrand[†], nothing has been done to determine the effect on the boiling-point of water produced by the presence of various quantities of salts dissolved in it. The vapour-pressure of water from salt-solutions of various strengths has also received but little attention; the results of Wüllner[‡], Babo, and one or two others comprising all that is known on this subject.

From the time when I began first to work at the subject of solution, it appeared to me that it was in this direction that most knowledge of the nature of solution was to be gained; but it is only recently that I have been able to turn my attention to this point. The following pages contain an account of my experiments on the pressures under which saturated salt-solutions boil at different temperatures. These experiments are merely preliminary to a more extended and more accurate series of determinations of the pressure of aqueous vapour from such solutions. Still the results of these first attempts

are so striking and so totally at variance with all received ideas on this subject, while they agree so completely with the theory of solution put forward by me in the paper of which this is the continuation*, that I feel they possess sufficient interest, and are of sufficient importance, to warrant their publication.

My method of experiment is as follows :—

A wide test-tube A, 200 millim. by 30 millim., is fitted with an india-rubber cork through the centre of which passes a thermometer B. By a hole at the side of the thermometer is attached the upright condenser C: this is made of thin-walled wide glass tube, and is surrounded with a cylinder through which cold water flows ; the upper end of the condenser communicates with the T-piece D, one arm of which has a stopcock, and the other is connected with a piece of capillary tubing E, 100 millim. long and about ·3 millim. in internal diameter; this in its turn is joined to the gauge F, and has a stopcock H by means of which the whole may be placed in communication with the atmosphere. The gauge stands side by side, in a trough of mercury, with a barometertube G in front of a mirror-scale divided into millimetres, the pressure of the vapour in A being given by the difference in height of the mercury in G and F. In making an experiment, a quantity of salt along with a piece of granulated zinc
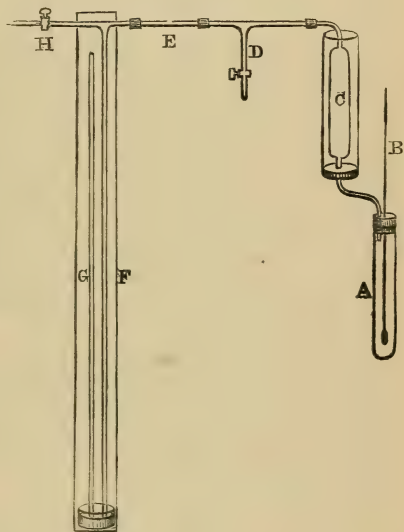
or tin is introduced into A, and water sufficient to rather more than cover the bulb of the thermometer is then added. The quantity of salt is so great that some of it remains undissolved at the highest temperature reached during the experiment. The tube is then placed in position and surrounded by a bath of water, the temperature of which is governed by a thermostat. The temperature of the water is then raised to

5° above the point at which the vapour-pressure is to be
determined.   The temperatures at which determinations were
made were 65°, 75°, 85°, 95°, as indicated by the thermo-
meter B.   The temperatures of the bath were therefore respec-
tively 70°, 80°, 90°, and 100°.   The temperature of the bath
having become constant, the stopcock H is closed and D is
opened, communication with a water-pump being thus estab-
lished.   As soon as ebullition has commenced, D is closed and
opened occasionally till the reading of B is one degree or so
lower than the temperature of experiment.   After steady boil-
ing for some time, H is momentarily opened; the temperature,
as indicated by B, rises immediately a tenth or so: in this way
the temperature of ebullition is slowly raised till the desired
point is reached.   The heights of F and G are then read, and
one observation is completed.   D is again opened and closed
and the whole operation repeated; and the mean of the two
differences in height of the mercury in F and G is entered as
the pressure of water-vapour at $t°$ from the salt-solution
saturated at $t°$.   Two observations are also made with another
quantity of the same salt.   Thus the results entered in the fol-
lowing tables are based on four determinations.   The use of
the capillary E is to deaden the oscillation of the mercury in
F, which would otherwise be produced by the brisk ebullition
in A.   Thus the reading of F gives the mean of the momen-
tary pressures in A, as the thermometer shows the mean of
the momentary temperatures.   The piece of granulated zinc
or tin is added to obviate bumping; and it is practically un-
attacked, as only a trace of dissolved metal could be detected
after even four hours' boiling.

As these experiments were merely tentative, no attempt was
made to correct the temperature-readings nor the readings of
the barometer; and necessity for this was to a great extent
removed by making a series of observations with pure water
and comparing the results with the figures calculated from
Regnault's experiments.

Table I. contains the figures I obtained from two sets of
double determinations.   As is seen from it, my results are
uniformly lower than Regnault's by $7·25 ± ·5$; but as no
attempt was made to read closer than ·5 millim., the con-
cordance is satisfactory; and it is only necessary to apply as
corrections the numbers in the difference-column to the
pressures of water-vapour of salt-solutions afterwards given,
to obtain the true pressures at the true temperatures.

In Table II. are given the results I obtained corrected as
above, and the temperatures to which these pressures of

TABLE I.

t°.	p_1 and p_2.	Mean p.	p' (Regnault).	Difference.
$\overset{\circ}{65}$,,	180 180	180	186·9	− ·6·9
75 ,,	281·5 280·5	281	288·5	−7·5
85 ,,	426 426·5	426·3	433	−6·7
90 ,,	626 626	626	633·8	−7·8

TABLE II

Salt.	t.	p.	p cor.	t'.	$t - t'$.
NaNO$_3$	$\overset{\circ}{65}$ 75 85 95	114·0 172·0 249·7 355·0	120·9 179·5 256·4 362·8	$\overset{\circ}{55}$·6 64·1 72·2 80·5	$\overset{\circ}{9}$·4 10·9 12·8 14·5
KNO$_3$	65 75 85 95	...... 213·5 308·0 419·3	...... 221·0 314·7 427·1	...... 68·8 77·1 84·6	...... 6·2 7·9 10·4
Na$_2$CO$_3$	65 75 85 95	148·0 232·0 357·7 529·0	154·9 239·5 364·4 536·8	60·9 70·6 80·6 90·5	4·1 4·4 4·4 4·5
K$_2$CO$_3$	65 75 85 95	...... 116·0 166·0 237·0	...... 123·5 172·7 244·8	...... 56·0 63·2 71·1	...... 19·0 21·8 23·9
MnSO$_4$	65 75 85 95	160·3 249·0 388·0 584·0	167·2 256·5 394·7 591·8	62·5 72·1 82·6 93·1	2·5 2·9 2·4 1·9
FeSO$_4$	65 75 85 95	158·8 251·8 386·0 580·0	165·7 259·3 392·7 587·8	62·3 72·4 82·5 93·0	2·7 2·6 2·5 2·0
KNO$_3$ Same strength.	65 75 85 95	146·0 224·0 335·0 491·5	152·9 231·5 341·7 499·3	60·6 69·8 79·1 88·7	4·6 5·2 5·9 6·3
FeSO$_4$ Same strength.	65 75 85 95*	163·0 256·0 388·0 580·0	169·9 263·5 394·7 587·8	62·9 72·8 82·7 93·0	2·1 2·2 2·3 2·0

* Saturation took place at 90°.

aqueous vapour correspond. This is the usual method of expressing the action of a salt on the vapour-pressure of water—that is, it raises the boiling-point so many degrees.

It will be seen that the number of degrees that the boiling-point of water is raised is a quantity that increases with the temperature in all cases where the solubility also increases, but diminishes in a more or less marked manner when the solubility decreases with the rise of temperature. All this can be readily explained. It is only to be expected that the larger number of molecules of salt present should have a greater influence on the water-molecules; but this explanation fails when the case of KNO_3 of the same strength is examined. Here the quantity of salt remained the same, and yet the increase of rise of boiling-point is very well marked. That the strength of the solution was the same at the end as at the beginning of the experiment was proved by weighing the tube before and after : the loss of water and salt adhering to the thermometer did not amount to ·08 per cent. In this case, then, it appears that the restraining effect of the salt on the water increases with the rise of temperature.

Before attempting to explain this, I wish to draw attention to a much more convenient mode of expressing the action of salt on water with regard to its vapour-pressure. If at a temperature t the vapour-pressure of water is p_t, and at the same temperature the pressure of water-vapour from a salt-solution is p'_t, then the pressure of pure water is diminished by the salt $p_t - p'_t$ millim. Now as the value of p increases faster than the temperature, in order to compare $p_t - p'_t$ with $p_{t'} - p'_{t'}$ we must divide by pt and pt' respectively, giving us

$$1 - \frac{P't}{Pt} \text{ and } 1 - \frac{P'_{t'}}{Pt'}, \&c.,$$

numbers expressing the effect of the salt at those temperatures. If the salt-solution have the strength n molecules of salt to the 100 molecules of water, then $\dfrac{1 - \dfrac{P'}{P}}{n}$ expresses the effect of each molecule of salt at that particular temperature.

In Table III. are given the values of $\left(1 - \dfrac{P'}{P}\right) \times 10{,}000$ and the solubilities at the corresponding temperatures, with the values of $\dfrac{1 - \dfrac{P'}{P}}{n}$ also multiplied by 10,000. It is evident that the effect of rise of temperature on the attraction of salt for

water is to diminish it, as was to be expected, in the case of all the salts when in a saturated solution. But in the case of the

TABLE III.

Salt.	65°.	75°.	85°.	95°.	$\left(1 - \dfrac{P'}{P}\right) \times 10{,}000.$
NaNO₃	3667	3879	4142	4329	
KNO₃..........	......	2402	2775	3302	
Na₂CO₃	1778	1744	1609	1549	
K₂CO₃	......	5872	6106	6214	
MnSO₄	1094	1139	898	692	
FeSO₄	1178	1039	945	735	
KNO₃.........	1889	2028	2142	2149	
FeSO₄.........	944	890	899	735	
NaNO₃	27·1	29·86	32·82	36·21	mol.
,, ...	135·3	129·9	126·2	119·6	
KNO₃	22·08	27·59	33·65	40·24	mol.
,, ...	......	87·1	82·5	82·1	
Na₂CO₃	15·69	15·69	15·59	15·49	mol.
,, ...	113·3	111·1	103·3	100·0	
K₂CO₃	......	35·68	37·51	39·33	mol.
,, ...	......	164·5	162·8	158·0	
MnSO₄	14·76	14·76	14·71	13·89	mol.
,, ...	74·1	77·2	61·0	49·8	
FeSO₄	15·43	15·16	14·16	12·08	mol.
,, ...	76·3	68·6	66·7	60·9	

Solubility taken from Mulder (*Bijdragen tot de Geschiedenis van het scheikundig gebonden Water* (Rotterdam, 1864).

solutions of constant composition the attraction of salt for water is increased with KNO₃, and diminished with FeSO₄; and this is also found with MnSO₄ at the temperatures 65° and 75°—so long as the solubility remains constant the value of $1 - \dfrac{P'}{P}$ increases. Now KNO₃ has its solubility largely increased by rise of temperature, while that of FeSO₄ is diminished; and we have seen above that when $n = \text{constant}$, $1 - \dfrac{P'}{P}$ increases in the case of KNO₃ and diminishes in the case of FeSO₄. The explanation of this apparently anomalous behaviour must lie in a change in the molecular relations in the solution. I have stated in previous papers that, from other experiments, I have come to the conclusion that the solubility of a salt is dependent on the attraction of salt for water and of salt for salt : if the former increases faster than the latter with the rise of temperature, then the salt is more soluble at a high temperature than at a lower, and *vice versâ*. Now in

a strong solution the molecular volume of each salt-molecule is greater than it is in a weak solution, owing to the attraction of salt for salt having to a certain extent overcome the attraction of salt for water. If, however, the solubility of the salt increases with rise of temperature, then the effect of heat will be to weaken to a great extent the attraction of salt for salt, and to a small extent that of salt for water; but the diminution in the attraction of salt for salt may be so great as to be practically equal to an *increase* of the attraction of salt for water; and such is the case with the solution of KNO_3 given above. On the other hand, when solubility decreases with rise of temperature, then the attraction of salt for water diminishes faster than that of salt for salt ; and this is to be seen in the case of $FeSO_4$ above.

Some experiments I have made on the coefficient of expansion of concentrated solutions will make this even more clear. I experimented with NaCl, KCl, $NaNO_3$, and KNO_3 in nearly saturated solutions at 20°, and determined their density at 20°, 40°, and 98° C. The results and approximate strengths of the solutions are given in Table IV.; and the volumes at

Table IV.

Salt.	δ 20°.	δ 40°.	δ 98°.	n.
NaCl	1·19987	1·19614	1·19939	10·5 (*c*)
KCl	1·1827	1·18073	1·18602	8·5 ,,
$NaNO_3$	1·14573	1·14107	1·13763	5·5 ,,
KNO_3.........	1·17311	1·16906	1·16668	5+

Water at 20°, 40°, and 98° taken as unity.

Density referred to Water at 20° and Volumes.

Salt.	t°.	δ_{20}.	Volume.	Volume − vol. of water.
NaCl	20	1·19987	100,000	
	40	1·18911	100,905	+312
	98	1·15349	104,021	+ 42
KCl	20	1·1827	100,000	
	40	1·17374	100,763	+170
	98	1·14063	103,688	− 291
$NaNO_3$ ...	20	1·4573	100,000	
	40	1·13435	101,004	+411
	98	1·0941	104,720	+741
KNO_3......	20	1·17311	100,000	
	40	1·16217	100,941	+348
	98	1·12203	104,552	+573

these temperatures (volume at $20° = 100,000$) are compared with the volume of water at the same temperature, that of water being taken as follows:—

$$\begin{aligned}
\text{At } 20° &= 100,000, \\
,, \ 40° &= 100,593, \\
,, \ 98° &= 103,979.
\end{aligned}$$

Thus it is seen that, comparing the expansion between $20°$ and $40°$, or $20°$ with that between $40°$ and $98°$ or 58 degrees, that of water is about as $1 : 6$, while in all the salt-solutions it is less than $1 : 1$; and in the case of KCl the volume at $98°$ is very considerably less than that of water, contraction having taken place between $40°$ and $98°$. This has also been observed by Kremers, as I have shown in a previous paper[*], and the table of molecular volumes at $20°$ and $40°$ that I have already published[†] also fully bears this out; so that it is clear that, in a strong solution, the effect of rise of temperature is to cause an expansion which, as the temperature rises, becomes more and more similar to that of water alone, and after that actually is considerably less than it; so that at a high temperature the volume may be even less than that of water.

Thus the experiments on the vapour-pressures of salt-solutions of constant strength, and on the coefficient of expansion of such solutions, show most plainly that, by rise of temperature, the attraction of salt for salt is so greatly diminished that it is equivalent to an increase in attraction of salt for water. That this is not the case with constantly saturated solutions is due to the attractions of salt for water and of salt for salt being in such solutions in equilibrium. Thus the effect of heat is, as usual, to diminish the attraction of salt for water, as is shown by the diminution of the value $\dfrac{1 - \dfrac{P'}{P}}{n}$.

It is by a comparison of the values of $\dfrac{1 - \dfrac{P'}{P}}{n}$ for various salts at the same temperature that I hope to be able to arrive at the comparative value of the attraction of water for salt, the second factor in solution, while the ratios of the fraction F[‡] give the comparative values of the attraction of salt for salt.

* Phil. Mag. February 1883. † Ibid. August 1883.
‡ "Saturation of Salt-Solutions," Phil. Mag. June (Supplement) 1884.

XXXIX. *On a Method of Calculating the Constant* γ, *expressing the Relation of the Specific Heat at Constant Pressure to the Specific Heat at Constant Volume. By* W. Moon[*].

LET H_1 equal the specific heat of air at constant pressure, and H the specific heat at constant volume; then, when a volume of air is compressed through dv, the adiabatic pressure of the air will be $1 + \dfrac{1}{v} dv \dfrac{H_1 - H}{H}$ times the isothermal pressure; and if this value is equated with the pressure calculated from the work required to produce the compression, then the value of $\dfrac{H_1}{H}$ may be ascertained without experimentally knowing the value of H.

The pressure may be thus calculated from the work required to produce the compression:—

If the temperature of a volume of air is increased from t to t_1 (the volume being constant), then the pressure of the air will be increased from 1 to $\dfrac{1 + t_1 \cdot 003665}{1 + t \cdot 003665}$; and therefore if, while the volume of air is compressed from 1 to $\dfrac{1}{v}$, the temperature of the air varies from t to t_1, then the pressure of the air will be

$$\frac{h}{760} \, 1033 \cdot 796 \left(\frac{1 + t_1 \cdot 003665}{1 + t \cdot 003665} \right) \frac{1}{v} \text{ grammes,}$$

where $h =$ barometric height, and $1033 \cdot 796$ the pressure upon a square centimetre at 760 millim.

The heat given off in the gas is equal to the work performed against the gas in compressing it divided by Joule's equivalent. Therefore, when the air is compressed through dv, the heat given off

$$= \frac{\dfrac{h}{760} \, 1033 \cdot 796 \left(\dfrac{1 + t_1 \cdot 003665}{1 + t \cdot 003665} \right) \dfrac{1}{v} dv}{42355} \text{ calories.}$$

To obtain from this expression the increase of temperature of the air, it must be divided by the specific heat at constant volume and the weight of a cubic centimetre of air,

$$= \frac{\dfrac{\dfrac{h}{760} \, 1033 \cdot 796 \left(\dfrac{1 + t_1 \cdot 003665}{1 + t \cdot 003665} \right) \dfrac{1}{v} dv}{42355}}{\dfrac{H}{H_1} \cdot 2375 \times \cdot 001293187 \dfrac{h}{760} \dfrac{1}{1 + t \cdot 003665}} \left\{ \begin{array}{l} \text{degrees} \\ \text{Centigrade.} \end{array} \right.$$

By reducing, this equals

$$\frac{H_1}{H}\ 79{\cdot}47\ (1 + t_1{\cdot}003665)\frac{1}{v}\,dv \text{ degrees Cent.,}$$

which equals the increase of temperature of the air resulting from its compression; and from this value the increase of pressure resulting from the increase of temperature may be calculated, since air tends to expand ·003665 of its volume for each increase of a degree Centigrade beyond zero.

$$\therefore\ \frac{1 + \left\{ t_1 + \dfrac{H_1}{H}\,79{\cdot}47(1 + t_1{\cdot}003665)\dfrac{1}{v}\,dv\ \right\}\cdot003665}{1 + t_1{\cdot}003665}$$

$$=\frac{(1 + t_1{\cdot}003665)\left(1 + \dfrac{H_1}{H}{\cdot}79{\cdot}47 \times {\cdot}003665\,\dfrac{1}{v}\,dv\right)}{1 + t_1{\cdot}003665}$$

$$=1 + \frac{H_1}{H}\cdot29126\frac{1}{v}\,dv.$$

Therefore when a volume of air is compressed through dv, it acquires a pressure adiabatically; that is $1 + \dfrac{H_1}{H}\cdot29126\dfrac{1}{v}\,dv$, e pressure the air would have if compressed isothermally.

By equating this value with $1 + \dfrac{H_1 - H}{H}\dfrac{1}{v}\,dv$, the value of $\dfrac{H_1}{H}$ may be obtained; since

$$1 + \frac{H_1}{H}\cdot29126\frac{1}{v}\,dv = 1 + \left(\frac{H_1}{H} - 1\right)\frac{1}{v}\,dv\ ;$$

$$\therefore\ \frac{H_1}{H}\cdot29126 = \frac{H_1}{H} - 1;$$

$$\therefore\ \frac{H_1}{H} = \frac{1}{1 - {\cdot}29126} = 1{\cdot}41095.$$

So that the value of $\dfrac{H_1}{H}$ or γ, determined by this method, would appear to be about 1·41.

XL. *On Contrariants, a New Species of Invariants.* By
J. J. SYLVESTER, *F.R.S., Savilian Professor of Geometry in
the University of Oxford*[*].

"Non notationes sed *notiones* novæ desunt."

ALL algebraists of the new school are familiar with the
use of contrariants derived from and, so to say, sub-
ordinate to, one or more primordial forms; but I am not aware
that, previous to my researches into the theory of the linear
equation in matrices, published in recent numbers of the
Comptes Rendus, any one has ever had occasion to consider
algebraical forms perfectly independent of, and given coordi-
nately as contravariantive to, one another. An invariant of
two such forms or systems of forms is called a Contrariant.

It is no new circumstance in Mathematical History for a
general doctrine to take its rise in some process applied to a
particular investigation. It is a fact, but one not generally
known in this country, that the Cartesian method of coordi-
nates originated in a happy idea which occurred to Descartes,
how to solve completely a geometrical problem bequeathed to
posterity by Pappus, apparently without any design on the
part of its immortal author to create a new geometrical cal-
culus. So much is this the case, that some who have studied
that enigmatic treatise Descartes' *Géométrie* have come to
the conclusion that it was designed rather with the view of
applying geometry to algebra and obtaining graphical solu-
tions of equations, than with that of reducing geometrical
analysis under the dominion of algebraical methods. With
the object of familiarizing my fellow workers with the novel
and (as the researches above alluded to demonstrate) im-
portant conception, which at one stroke doubles the area of
invariantive theory and its geometrical applications, I propose
to consider the complete system of irreducible contrariants
to two quadratic forms with any number of variables.

Another simple and interesting problem will be to show how
to transform simultaneously two contravariantive quadratics
(of course by contragredient substitutions) into one and the
same sum of powers of the substituted variables; but this
must be reserved for some future occasion.

The fundamental or irreducible invariants of two covarian-
tive quadratics, say f and ϕ, of n variables we know are $n+1$
in number (being the coefficients of the binary Quantic in λ, μ,
obtained by supplying the same system of variables to the two
forms f and ϕ and then taking the discriminant of $\lambda f + \mu \phi$),

and will be of the deg . degs $n, 0$; $n-1, 1$; $n-2, 2$; ... $1, (n-1)$; $0, n$ respectively.

I shall show that the same two forms, when treated as contravariantive, are also $n+1$ in number ; viz. two, as before, of the deg . degs $n, 0$; $0, n$; and the rest of the deg . degs $1, 1$; $2, 2$; $3, 3$; ... ; $(n-1), (n-1)$.

The proof is instantaneous, or nearly so ; for by two contragredient substitutions, f and ϕ may be transformed into $a_1 x_1^2 + a_2 x_2^2 + \ldots + a_n x_n^2$ and $k\xi_1^2 + k\xi_2^2 + \ldots + k\xi_n^2$ (where the k is employed in lieu of unity as a safeguard for maintaining homogeneity in the subsequent operations). If, now,

$$\frac{d}{dx_1}, \quad \frac{d}{dx_2}, \quad \cdots \quad \frac{d}{dx_n}$$

be written in lieu of

$$\xi_1, \quad \xi_2, \quad \cdots \quad \xi_n$$

in the second form, and this form so modified and its successive powers be made to operate upon the first form and its corresponding powers, it is obvious that by combining the results of these operations, we may obtain the invariants

$$\Sigma k a_1 ; \quad \Sigma k^2 a_1 a_2 ; \quad \ldots ; \quad \Sigma k^{n-1} a_1 . a_2 \ldots a_{n-1} ;$$

in addition to which we have the invariants of the two forms taken separately, viz. $a_1 . a_2 \ldots a_n$ and k^n.

These $n+1$ invariants are, upon the face of them, mutually independent.

But any invariant of the two forms must be symmetrical in regard to the a's, and consequently must be a symmetrical function of

$$\Sigma k a_1, \Sigma k^2 a_1 a_2 ; \quad \ldots ; \Sigma k^{n-1} a_1 . a_2 \ldots a_{n-1} ; \quad a_1 . a_2 \ldots a_n,$$

say F ; or at all events of the form $k^{\pm\theta}$ F, where θ is an integer less than n ; but in such case $k^{\pm\theta}$ will be a rational (I do not say integral) invariant of the system, and therefore of the second form of the system, which we know has no other invariant than powers of k^n. Hence $\theta = 1$, and consequently there are no invariants other than the $n+1$ independent ones above given. These, then, are the irreducible contrariants ; and it may be noticed that the sum of their deg . degs is $\frac{n^2+n}{2}$, $\frac{n^2+n}{2}$, the same, *i. e.*, as the like sum for the irreducible invariants of the same two forms regarded as covariantive.

An ordinary invariant might, in analogy with botanical language, be termed Invarians Vulgaris, or Simplex, or Eisensteinensis (from the name of the first discoverer of the species) ; and so a Contravariant, which necessarily belongs

to two forms or two systems of forms, might be called Invarians Duplex, or Versicolor, or after the name of the person who first imported the notion of contragredience into the subject.

A *simple* invariant may be likened to a monocotyledonous, a *contrariant* to a dicotyledonous plant. And, again, an assembly of forms containing a system of covariantive sets of variables may be regarded as a monogamous, one containing a system of sets partly covariantive and partly contravariantive, as a digamous complex; and in the latter case there will be the further distinction into diœcious or monœcious; for the two kinds of systems of variables may be confined to separate forms, or appear together in the same mixed form, or they may occur together in some of the forms and separate in the others.

In order to illustrate the position that such kind of analogies are not purely fanciful, but have their origin in the Unity of Nature, alike in its intellectual and its physical manifestations, let me be allowed to recall the instance that I was led *à priori* by a somewhat similar parallelism to anticipate a biological possibility, which my distinguished colleague Prof. Martin, of the Johns Hopkins University, was good enough to point out to me is an actual fact in nature connected with Darwin's theory of superfluous males. See "Constructive Theory of Partitions," American Journal of Mathematics, vol. vi. footnote to the *Exodion*.

New College, Oxford,
    September 17, 1884.

XLI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 229.]

May 14, 1884.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

THE following communications were read:—
    1. "On the Pre-Cambrian Rocks of Pembrokeshire, with especial reference to the St. David's District." By Dr. Henry Hicks, F.G.S., with an Appendix by Thomas Davies, Esq., F.G.S.

The author, in this paper, gave further detailed evidence in addition to that already submitted by him, to show that the Geological Survey Map of the district of St. David's and of other parts of Pembrokeshire is incorrect in some of its most essential features, and inaccurate in very many of its petrographical and stratigraphical details. Some new areas in South Pembrokeshire were also referred to. He

replied also to the criticisms contained in the paper by the Director-General of the Survey, read last year before the Society, and indicated that Dr. Geikie had completely misunderstood the sections and the order of succession of the rocks at St. David's. He pointed out that the views so elaborately worked out by the Director-General, to show the evidence of metamorphism in the rocks, were based on the entirely false supposition that the granitoid rocks were intrusive in the Cambrian rocks, and that the felsites were merely peripheral masses. He showed, by producing abundant fragments of the granitoid rocks and of the felsites from the basal Cambrian conglomerates, that the granitoid rocks were the very oldest rocks in the district, and that they must undoubtedly be of Pre-Cambrian age. He proved, from microscopical evidence, that the rocks supposed to have been altered by the intrusion of the granitoid rocks, were in the condition in which they are now found before the Cambrian rocks were deposited, and, moreover, that the supposed concretions in the porcellanites and conglomerates, claimed to have been due to metamorphism, had turned out, on microscopical evidence, to be actually fragments of old Pre-Cambrian rhyolites enclosed in the sediments. It was shown also that at the points indicated by the Director-General, where the evidences of intrusion were supposed to be seen, there was not the slightest change of a metamorphic character induced in the sedimentary rocks in contact with the granitoid rocks. The only difference that could possibly be recognized in them by the aid of the microscope was such as is well known to be the result of crushing when in the neighbourhood of faults. Indeed there was the clearest evidence possible to show that the junctions were merely fault junctions. The supposed fold in the Pebidian rocks, the author stated, was impossible if petrological evidence was of any value. The author also produced many facts to show that the conglomerates at the base of the Cambrian constantly overlapped the different members of the series which he claimed to be of Pre-Cambrian age, and that the unconformity was very marked and to be clearly seen in many coast-sections. The conglomerates were shown also to contain well-rolled pebbles of all the series included under the names Dimetian, Arvonian, and Pebidian, as proved by careful microscopical examination of the fragments by Mr. T. Davies and himself. An Appendix, by Mr. Davies, describing the microscopic character of the rocks accompanied the paper.

2. " Note on a specimen of Iron Amianthus." By the Rev. J. Magens Mello, M.A., F.G.S.

The accompanying specimen was found at the bottom of one of the Wingeworth iron-furnaces, near Chesterfield, and was given to me by Mr. Arthur Carrington, one of the owners.

The furnaces have been lately blown out for repairs, and in the mass of slaggy refuse at the bottom a thin layer of the curious product known as Iron Amianthus was interposed between the sand and the iron refuse.

The red sand at the bottom of the furnace was converted in its upper part into a compact hard white sandstone, an inch or two in

thickness, and upon the top of this the Iron Amianthus occurred in snow-white fibrous masses, the fibres radiating in a concentric manner, and forming more or less botryoidal concretions, somewhat resembling hæmatite in appearance, and separated by extremely thin plates or septa of iron, by which the entire mass is divided into irregular prisms of about half an inch in diameter.

A similar product is described by Percy as occurring in the blast-furnaces of the Harz, and is said to consist almost entirely of fibrous silica, with a few specks of iron and graphite, and minute cubes of nitro-cyanide of titanium. Both graphite and titanium occur in the Wingeworth refuse; the graphite is found in thin plates, the nitro-cyanide of titanium in masses of crystals.

Percy states that the origin of the Iron Amianthus is found in the oxidation of the silicon, which is separated in greater or less degree under the same conditions as graphite, and is oxidized at a high temperature.

May 28.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

The following communications were read :—

1. "The Archæan and Lower Palæozoic Rocks of Anglesey." By Dr. C. Callaway, F.G.S. With an Appendix on some Rock-specimens, by Prof. T. G. Bonney, D.Sc., F.R.S., President G.S.

The object of the author was to furnish additional proof of the Archæan age of the altered rocks of the island. He held that the Pebidian mass on the north was fringed by Palæozoic conglomerates, containing, amongst other materials, large rounded masses of limestone, derived from the calcareous series on the north coast, these conglomerates being probably a repetition by reflexed folding of those which lie at the base of the Palæozoic series. In like manner conglomerates which margined the western (Holyhead) schistose area contained angular pieces of altered slate undistinguishable from some of the Pebidian rocks of the north-west. These conglomerates dipped to the east, forming the western side of a syncline. Near Llanfihangel were sections which showed not only the Archæan age of the gneissic and slaty (Pebidian) groups, but also the higher antiquity of the former. These conclusions were derived from the occurrence of granitoid pebbles in the slaty series, and from the presence of masses of the slate, as well as gneissic fragments, in the basement Palæozoic conglomerates. The author was at present unable to accept the Cambrian age of the lower Palæozoic rocks, and considered that the fossils he exhibited tended to confirm the views of the Survey on the correlation of those strata. The paper concluded with a sketch of the physical geography as it probably existed in Ordovician times. An Appendix furnished by Prof. Bonney tended, by microscopic evidence, to confirm the proof furnished by the paper.

2. "On the new Railway-cutting at Guildford." By Lt.-Col. H. H. Godwin-Austin, F.R.S., F.G.S., and W. Whitaker, Esq., B.A., F.G.S.

In this paper the authors described a section exposed in a new

railway-cutting just north of Guildford station. The beds exposed are Chalk and Eocene strata at the base, with overlying Pleistocene or drift-beds. The Eocene beds appear at each end of the cutting, the London Clay resting upon Woolwich and Reading beds as described in 1850 by Prof. Prestwich ; and the interest of the section is due in part to this exposure of the Woolwich and Reading beds, which are rarely seen in this neighbourhood, and in part to the thick mass of Pleistocene clays and gravels overlying the lower Tertiary deposits. The latter appear to be only the remnants of more extensive deposits in the gorge of the Wey, which were spread over the area to the north before the river had cut down to its present level. Some of them are in part of fluviatile origin and composed of materials derived first from the Lower Greensand and afterwards from the Chalk, ironstone predominating in the former and flints in the latter. Resting unconformably upon these are deposits consisting of irregularly bedded coarse loamy sands, beds of large flints, with an admixture of fragments of chalk, and with nests or large lumps of red clay. These are regarded as glacial beds, and in the sands beyond the bridge at the London Road remains of Mammalia (*Elephas* &c.) were found ; these sands are exposed as far as Watford farm, where they terminate abruptly against a steep bank of Woolwich and Reading beds. On digging through them at this point the dark gravels with greensand ironstone were met with.

The authors pointed out that the most interesting questions connected with these high-level gravels and sands of the ancient Wey are as follows :—1. What was their relation to the topography of the country in the past ? 2. What relation do they bear to the outlines of the country at the present day ? 3. What is their age ?

They showed that when the gravels and sands were deposited the main drainage of the country was the same as it now is, though the river was 60 feet above its present level. The sands with mammalian bones were probably an accumulation in a re-entering bend of the river, similar to one now existing a little further north. The river appears at first to have been more rapid, when the lower ironstone gravels were deposited, then slower, when the sands accumulated. Some change of levels ensued, and a considerable portion of the deposits was removed before the upper strata of loam and flints were formed. It is probable that the gorge of the Wey was no longer an outlet to the north whilst these beds were being deposited. In general the loam and flint beds are horizontal, whilst in some localities they are displaced in a manner remarkably like what is seen in the glacial deposits of Alpine valleys. They contain land-shells in places. The land surface indicated by the lower gravels and sands at Guildford is of older date than that described by Mr. R. A. C. Godwin-Austen in the country to the southward, and especially in the valley of the Tillingbourne.

The deposits near Guildford belonging to the two epochs were noticed in some detail. Both are pre-glacial and have been formed when the climate was temperate. The overlying glacial deposits formed of chalk-detritus, flints, and loam are attributed to the

action of land ice, and the probable effects of a low temperature are described and illustrated by those observed on the plateaus around Chang Cheumo in Tibet.

3. " On the Fructification of *Zeilleria* (*Sphenopteris*) *delicatula*, Sternb., sp., with remarks on *Ursatopteris* (*Sphenopteris*) *tenella*, Brongn., sp., and *Hymenophyllites* (*Sphenopteris*) *quadridactylites*, Gutb., sp." By R. Kidston, Esq., F.G.S.

4. " On the Recent Encroachment of the Sea at Westward Ho!, North Devon." By Herbert Green Spearing, Esq. Communicated by Prof. Prestwich, M.A., F.R.S., V.P.G.S.

The author stated that for the last nine years the sea has encroached near Westward Ho ! at the rate of about 80 feet annually. The encroachment affects only about a mile of the coast-line, but the sea has gradually worn away part of the Northam Burrows—a sandy common forming the southern portion of the united delta of the Taw and the Torridge,—and partially removed a broad ridge of pebbles which formerly defended the coast-line, the pebbles of which, derived from a raised beach, travel in a northerly direction towards the mouth of the river. The sea tends to cut a way through the lower part of the Burrows, isolating part of the pebble ridge and forming a new mouth to the river. The inroads of the sea have laid bare a submerged forest, composed chiefly of oak, birch, and hazel, and containing bones of ox, sheep, deer, dog, pig, and goat, with flint cores and chips, and shells of oysters, limpets, periwinkles, &c. The woody layer, 18 or 20 inches thick, can be traced for 400 yards to extreme low-water mark ; it rests on blue clay, which is 4 feet thick under the pebble-ridge, but thins to seaward. It contains estuarine shells. Below it is a layer of rounded pebbles. Near the mouth of the river patches of shelly sandstone rest on the clay, resembling that seen near Croyde, on the north side of the bay.

In 1874 a pebble beach sloped to the sea from the frontage of the building land at Westward Ho ! The pebbles have now disappeared, and a cliff of clay, 15 feet high, occupies the spot. Near the Ladies' Baths this clay rests on rock of Carboniferous age, but nearer the Burrows, to the northward, a layer of sand intervenes, and, being easily washed away, facilitates the removal of the clay. To the north and east the clay thickens and is mixed with pebbles, many of which are broken. This may be due to glacial action, but no scattered stones have been observed. So long ago as 1600–1630 records of encroachments exist.

5. " On further Discoveries of Footprints of Vertebrate Animals in the Lower New Red of Penrith." By George Varty Smith, Esq., F.G.S.

June 11.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

The following communications were read :—

1. " The Range of the Palæozoic Rocks beneath Northampton." By Henry John Eunson, Esq., F.G.S.

The author referred to a shaft sunk at Kingsthorpe, near North-

ampton, in 1836, and also to a boring at the London and North-Western Railway-Station about ten years later. At these spots the beds beneath the Liassic series consisted of sandstones and marls, and were considered to be of Triassic age.

Palæozoic rocks were met with in two borings undertaken by the Northampton Water Company, who attempted to reach the Water-stones by piercing the upper beds of the Trias. The first boring was situated between the sites of the two previous investigations, on the Kettering road, near the town. The Upper, Middle, and Lower Lias here attain a thickness of 738 feet, and below them a series of conglomerates, sandstones, and marls rested upon an eroded surface of a Carboniferous dolomite which passed into limestone crowded with characteristic fossils. The beds above the dolomite are not true Trias, but may represent local deposits of that age; 46 feet of Carboniferous strata were drilled, and the boring was discontinued at 851 feet.

The second boring was at Gayton, five miles south-west of Northampton. The Middle and Lower Lias were 581 feet in thickness, and were succeeded by the White Lias and Rhætic shales, the latter containing the black shales and bone-bed. The Trias was here discovered, but only 60 feet in thickness, the Water-stones being absent. Then followed 20 feet of littoral beds containing fragments of Carboniferous Limestone (from which more than 20 species of fossils were named by Mr. R. Etheridge, F.R.S.), resting, at 699 feet, upon an eroded surface of Carboniferous Limestone, dipping at an angle of 45°, but in what direction was not ascertained. The beds between this point and 889 feet consisted of a series of limestones and dark shales 79 feet, grey sandstones and grits 40 feet, red marls and sandstones 71 feet. The last fossils were observed at 889 feet. The boring was continued to a depth of 944 feet. The last 105 feet was composed of coarse red sandstones and marls with several bands of hard grits. These grits had been examined microscopically by Prof. Bonney, whose notes were given. The above series may represent the Old Red Sandstone, or may be only a local development of the lower beds of the Carboniferous; however their materials have probably been derived from a mass of granitoid rocks belonging to some of the most ancient in the Archæan series. Saline water was met with in both borings.

A description was also given of an unsuccessful boring for coal at Orton, near Kettering. Beneath the Lias clays, 666 feet in thickness, the White Lias and Rhætic were discovered, followed by a sandstone and breccia resting upon an eroded surface of a quartz-felsite at 715 feet. The boring was discontinued at a depth of 789 feet in this rock. The quartz-felsite had been examined by Prof. Bonney, who expressed an opinion that it was similar to rocks of the volcanic group of Charnwood Forest, 25 miles to the north-east. The old land surface had thus been proved at the three borings, at Gayton dipping rapidly, and probably being the edge of a syncline, in which coal may yet be discovered to the south or south-west, beneath the overlying Mesozoic formations.

2. "On some Zaphrentoid Corals from British Devonian Beds."
By A. Champernowne, Esq., M.A., F.G.S.

3. "On the Internal Structure of *Micrabacia coronula*, Goldf.
sp., and its Classificatory Position." By Prof. P. Martin Duncan,
M.B. (Lond.), F.R.S., F.G.S.

4. "A Correction in the assumed Amount of Energy developed by
the Secular Cooling of the Earth as stated in two Papers by the late
Robert Mallet, M.A., F.R.S., in the ' Philosophical Transactions,'
1874–75." By W. F. Stanley, Esq., F.G.S.

According to Mr. Mallet, the amount of heat lost from the initial
temperature of the earth will represent the force of its contraction.
To this force he attributes the inclination and crumpling of strata,
together with all volcanic phenomena. He states that the calcula-
tions of Elie de Beaumont, Forbes, and Sir William Thomson, 0·0065,
0·007, and 0·0085 millim. respectively, represent the thickness of a
plate of ice covering the earth, which, melted, would equal the heat
lost annually. From these data he calculates that from 575 to
777 cubic miles of ice, melted, would represent the loss of heat.
This calculation was shown to be entirely in error. According
to the data an amount of energy represented by the melting of
from ·7937 to 1·0387 cubic mile of ice only would be dissipated,
or about a 700th part of the amount estimated by Mr. Mallet.

June 25.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

The following communications were read :—

1. "Additional Notes on the Jurassic Rocks which underlie
London." By Prof. John W. Judd, F.R.S., Sec. G.S.

Since the reading of the former paper on the subject (February 6,
1884), the well-boring at Richmond has been carried to a depth
of more than 1360 feet. The point reached is, reckoning from
Ordnance-datum line, 220 feet lower than that attained by any
other boring in the London basin.

A temporary cessation of the work has permitted Mr. Collett
Homersham to make a more exact determination of the underground
temperature at Richmond. At a depth of 1337 feet from the sur-
face, this was found to be 75½° F., corresponding to a rise of tem-
perature of 1° F. for every 52·43 feet of descent.

The boring is still being carried on in the same red sandstones
and "marls," exhibiting much false-bedding, which were described
in the previous communication.

The Rev. H. H. Winwood, of Bath, has had the good fortune to
find the original fossils obtained by the late Mr. C. Moore from
the oolitic limestone in the boring at Meux's Brewery in 1878. A
careful study of these proves that though less numerous and in a
far less perfect state of preservation than the fossils from the Rich-
mond well, they in many cases belong to the same species, and
demonstrate the Great Oolite age of the strata in which they
occurred.

2. "On some Fossil Calcisponges from the Well-boring at Richmond, Surrey." By Dr. G. J. Hinde, F.G.S.

3. "On the Foraminifera and Ostracoda from the Deep Boring at Richmond." By Prof. T. Rupert Jones, F.R.S., F.G.S.

4. "Polyzoa (Bryozoa) found in the Boring at Richmond, Surrey, referred to by Prof. J. W. Judd, F.R.S." By G. R. Vine, Esq. Communicated by Prof. Judd, F.R.S., Sec. G.S.

5. "On a new Species of *Conoceras* from the Llanvirn beds, Abereiddy, Pembrokeshire." By T. Roberts, B.A., F.G.S., Woodwardian Museum, Cambridge.

6. "Fossil Cyclostomatous Bryozoa from Australia." By A. W. Waters, Esq., F.G.S.

7. "Observations on certain Tertiary Formations at the South Base of the Alps, in North Italy." By Lt.-Col. H. H. Godwin-Austen, F.R.S., F.G.S.

In a visit to some of the moraines on the south side of the Alps, the author's attention was drawn to certain Tertiary beds underlying the glacial deposits at Ivrea, and near the Lago d'Orta at Boca, Maggiora, and especially at Buccione, south of Orta, and close to the southern extremity of the lake. Here there is a small remnant of micaceous sands containing older Pliocene marine fossils. The species have been determined by Dr. Gwyn Jeffreys, and a list was appended to the paper. The patch of Pliocene beds has apparently been protected by the porphyritic mass on which the old tower of Buccione stands; the remainder of the Tertiary strata, which formerly must have extended northward to the Soce Valley, have been swept away by the ice of the glacial period.

The deposits at Boca and Maggiora were also described in some detail. They are probably newer Pliocene.

Near Ivrea the most interesting section seen was at Strambinello, on the banks of the Chiusella. Here on both banks of the stream horizontal Pliocene beds, containing marine shells, are exposed resting on diorite. On the south bank the Pliocene is broken up and mixed with diorite fragments. Moraine overlies the Pliocene. The great Dora Baltea glacier swept across the gorge of the Chiusella, and only left a remnant of the marine beds where protected by the ravine.

The Pliocene sea probably extended along the south base of the Alps, extending in long gulfs up the valleys, out of which the marine deposits have been swept by the ice, except in a few protected spots.

The paper concluded with a notice of some fossiliferous gritty marl seen in a ravine close to Dormiletto on Lago Maggiore. Although probably *in situ*, the mass was not sufficiently exposed to show its relations to the surrounding rocks.

8. "On the Geological Position of the Weka-Pass Stone." By Capt. F. W. Hutton, F.G.S.

The beds described in this paper are of older Tertiary and newer Secondary age, and occur in the northern part of Ashley county, in

the province of Canterbury, between the Hurunui and Waipara rivers. All of the beds are met with at Weka Pass, on the railway and road between Christchurch and Nelson, and the following is the section in descending order : —

1. Mount-Brown beds ; pale yellowish sandstone with bands of shells and coral limestone, considered by all New Zealand geologists Upper Eocene or Oligocene.
2. Grey sandy marl.
3. Weka-pass stone, yellowish with arenaceous limestone, usually with small green grains.
4. Amori limestone, white, flaggy, and argillaceous.
5. Green sandstone with remains of marine saurians.

The last rests conformably on beds of coal and shale, with leaves of dicotyledonous angiosperms, forming the base of the Waipara system. To this system Nos. 4 and 5 of the above section have also been referred by Dr. von Haast and the writer. The upper beds are the Oamara system of the same authors. The question to be decided is the limit between the two. The green sandstone (No. 5), and the coal shales, are generally admitted to be Cretaceous.

The geographical distribution of the beds enumerated was briefly described, the grey sandy marl (No. 2), the Amori limestone (No. 4), and the green sandstone having a northerly extension to Cook's Straits, whilst the other beds have been traced to the south only. An examination of the stratigraphical evidence shows that at Weka Pass, and also on the Waipara, the Weka-pass stone rests on a waterworn surface of the Amori limestone, and near the Pass the former overlaps the latter. The grey marl (No. 2) is evidently unconformable to the lower beds of the Waipara system, whilst at Waipara and Weka Pass it passes down conformably into the Weka-pass stone. The grey marl also passes up conformably into the Mount-Brown beds. The author concludes that the break in succession is between the Weka-pass stone and the Amori limestone.

The geological evidence is in accordance with the palæontological data. The fossils hitherto found in the Weka-pass stone (*Voluta elongata, Scalaria rotunda, Struthiolaria senex, Pecten Hochstetteri, Meoma Crawfurdi, Schizaster rotundatus,* and *Flabellum circulare*) are found in other parts of New Zealand in Upper Eocene beds. None of them are known from the Cretaceous Waipara system. The fossils from the grey marl are also in some cases identical with those found in the Mount-Brown beds.

The author concluded by giving reasons for not agreeing with Dr. Hector, who classes all the beds mentioned as belonging to one system of Cretaceo-Tertiary age.

9. " On the Chemical and Microscopical Characters of the Whin Sill." By J. J. H. Teall, Esq., F.G.S.

The Whin Sill is an intrusive sheet of basic igneous rock which occurs in the Lower Carboniferous strata of the north of England. It is remarkably uniform in character, the principal varieties evidently depending merely on the conditions of consolidation.

Close to the junctions the rock is compact; the dominant variety, however, is of a grey or bluish-grey colour and medium grain. Irregular masses of a very coarse variety, characterized by long flat prisms of pyroxene measuring an inch or more in length, occur here and there in the dominant medium-grained rock.

The principal constituents of the rock of the Whin Sill are plagioclase felspar, a pyroxene having certain special characters, and a magnetic titaniferous iron-oxide. Apatite is invariably present in very small quantity. Interstitial matter may generally be recognized, also in very small quantity; in the coarser varieties this interstitial matter takes the form of micropegmatite. The accessory constituents are a rhombic pyroxene (bronzite), hornblende, biotite, pyrite, and various green decomposition-products. Olivine has not been detected by the author, either as a fresh mineral or in the condition of a pseudomorph. The three principal constituents have been isolated by means of the Sonstadt solution and a weak barmagnet, and separate analyses are given in the paper. The felspar, if of one species, must be allied to andesine; the opaque iron-ore is strongly magnetic, and contains 33 per cent. of titanic acid. The prevailing pyroxene develops a laminated structure, parallel to the basal plane, by alteration. In composition it deviates in the most marked manner from the rule laid down by Tschermak, $Mg + Fe$ being greater than Ca. Bulk-analyses of two specimens of the Whin Sill were given, and one of these was calculated out by means of the data supplied by the separate analyses of the three principal constituents.

The rock presents many points of resemblance to the continental diabases. It comes nearest to certain Swedish diabases described by Törnebohm and to the great masses of trap which occur in the Mesozoic strata of the Atlantic border of North America.

10. "A Critical and Descriptive List of the Oolitic Madreporaria of the Boulonnais." By R. F. Tomes, Esq., F.G.S.

11. "On the Structure and Affinities of the family Receptaculitidæ, including therein the genera *Ischadites*, Murch. (= *Tetragonis*, Eichw.), *Sphærospongia*, Pengelly, *Acanthochonia*, g. n., and *Receptaculites*, Defr." By Dr. G. J. Hinde, F.G.S.

12. "On the Pliocene Mammalian Fauna of the Val d'Arno." By Dr. C. J. Forsyth Major. Communicated by Prof. W. Boyd Dawkins, F.R.S., F.G.S.

13. "Notes on the Geology and Mineralogy of Madagascar." By Dr. G. W. Parker. Communicated by F. W. Rudler, Esq., F.G.S.

This paper commenced with a sketch of the physical geography of the island of Madagascar. A central plateau from 4000 to 5000 feet high occupies about half the island, rising above the lowlands that skirt the coasts, and from this plateau rise in turn a number of volcanic cones, the highest, Ankaratra, being 8950 feet above the sea. With the exception of certain legends, there is no record of a period when the volcanoes were active: two such legends were given.

The known volcanic cones were enumerated. They extend from

the northern extremity of the island to the 20th parallel of south latitude. Beyond this granite and other primitive rocks occur as far as lat. 22°, south of which the central parts of Madagascar are practically unknown to Europeans.

Some crater-lakes and numerous hot and mineral springs occur.

Earthquakes are occasionally felt in the island, most frequently in the months of September and October. The shocks are generally slight.

Only a single trap-dyke is known near Antananarivo. The hills around this city are of varieties of granite (? granitoid gneiss). The general direction of the strata is parallel to the long axis of the island.

Marine fossils have been found by Rev. J. Richardson and Mons. Grandidier in the south-west part of the central plateau. These fossils are referred by the last-named traveller to the Jurassic system. Remains of *Hippopotami*, gigantic Tortoises, and an extinct Ostrich-like bird have also been recorded. North and north-west of the fossiliferous rocks, between them and the volcanic district of Ankaratra, sandstone and slate occur. North of this volcanic district again is a tract of country in which silver-lead (mixed with zinc) and copper are found.

Near the north-western edge of the central plateau are granitic escarpments facing northwards and about 500 feet high. Some details were also given of valleys through the central plateau and of lagoons within the coral reefs on the coasts. To these remarks succeeded some details of the physical features exhibited by the province of Imerina as seen from Antananarivo.

14. "Notes on some Cretaceous Lichenoporidæ." By G. R. Vine, Esq. Communicated by Prof. P. Martin Duncan, F.R.S., F.G.S.

XLII. *Intelligence and Miscellaneous Articles.*

THE INFRA-RED EMISSION-SPECTRA OF METALLIC VAPOURS.
BY H. BECQUEREL.

LAST year I submitted to the Académie des Sciences a short account of my first researches on the infra-red spectra emitted by metallic vapours, till then unknown [*]. Since that time I have investigated the subject still further by making use of a special spectroscope, which shall be described in a future paper; I will simply mention here, that the method consists in throwing the spectra, about to be examined, upon a suitable phosphorescent substance, which has been previously rendered luminous, and in observing the temporary excitation, which precedes extinction, under the influence of the infra-red rays. The lines and bands of the emission-spectra then appear brilliant, and can be examined with the microscope.

In experimenting on different phosphorescent substances, notably

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[*] *Comptes Rendus*, t. xcvii. p. 71.

certain preparations of sulphide of calcium, I found some much more sensitive than others for infra-red rays. These substances have permitted me to determine directly the wave-lengths for the more brilliant lines of several incandescent metallic vapours (potassium, sodium, cadmium), by using the diffraction-spectra produced by a very beautiful metal grating of Mr. Rutherfurd's, which was kindly lent me by M. Mascart.

For other metals, the spectra were obtained by means of a bisulphide-of-carbon prism. The positions of the lines were referred to those of the potassium and sodium lines, and to the positions of the bands and characteristic lines in the infra-red region of the solar spectrum, as well as the absorption-bands of samarium; the wave-length for each line was then determined by interpolation with great accuracy.

The wave-lengths for the lines and principal bands in the infrared of the solar spectrum have been again determined by means of the grating, which had been placed at my service; and the more sensitive substances in my possession have permitted me to extend these measurements much further than I was enabled to do in my previous researches *. I propose to return shortly to this work, which has led me to rectify several numbers relating to wavelengths at the less-refrangible end of the spectrum; I will only give here the wave-lengths of the principal lines used for reference: the band indicated by A″ in my former memoir is made up of two bands, whose wave-lengths are from 0·00115 to 0·00119 millim., and from 0·001132 to 0·001142 millim.; the large band A‴ extends from 0·001351 to about 0·001400 millim., and the extreme band A$^{\text{iv}}$ from 0·001800 to about 0·001900 millim. The wave-lengths of the characteristic absorption-bands of samarium, directly determined, are: from 0·001079 to 0·001097 millim. for the first, and from 0·001239 to 0·001267 for the second.

The metals were volatilized in the voltaic arc. The intensity was such, that I could make use of a very narrow slit, and observe, on the phosphorescent substance, interesting details. In this case, it is necessary that the image of the line be brought to an exact focus on the phosphorescent screen; for, unless this be so, the results are not observable when the slit is narrow. I have not as yet been able to invent a suitable arrangement for giving a complete and definite image of the whole of the infra-red spectrum; but, by repeated trials, it was possible to obtain sufficiently distinct images of the groups of lines which are to be examined. I am occupied, however, at the present moment with an improvement, which will admit of still greater delicacy.

The following table contains the wave-lengths for the most intense lines, bands, or groups of lines which characterize the spectra of several metallic vapours. The numbers are expressed in millionths of a millimetre, and are generally exact to one or two millionths of a millimetre.

* *Annales de Chimie et de Physique,* 5$^{\text{e}}$ série, t. xxx. p. 5.

Wave-lengths of the Principal Emission-Rays of several
Incandescent Metallic Vapours.

Wave-length.   POTASSIUM.

$\left. \begin{array}{l} 770 \\ 1098 \\ 1162 \\ 1233 \end{array} \right\}$ Lines very brilliant.

SODIUM.

$819 \left\{ \begin{array}{l} \text{Visible to the naked eye.} \\ \text{Capt. Abney has photographed this line and discovered} \\ \quad \text{that it is double.} \end{array} \right.$

1142.

$\left. \begin{array}{l} 870 \\ 961 \\ 1003 \\ 1034 \\ 1098 \end{array} \right\}$ STRONTIUM.

Lines and bands feebler ; approximate wave-lengths.

CALCIUM.

$\left. \begin{array}{l} 858\text{--}876 \\ 883\text{--}888 \end{array} \right\}$ Broad bands, probably groups of lines.

MAGNESIUM.

$\left. \begin{array}{l} 899 \\ 1047 \ (?) \end{array} \right\}$ Very intense, perhaps compound.
       Very feeble.

$\left. \begin{array}{l} 1200. \ \text{Broad and perhaps double.} \\ 1212 \end{array} \right\}$ This group resembles group *b*.

ALUMINIUM.

$\left. \begin{array}{l} 1128 \\ 1361 \cdot 5 \end{array} \right\}$ Broad and intense, perhaps compound.

$\left. \begin{array}{l} 1125 \\ 1306 \end{array} \right\}$ ZINC.

1050.   CADMIUM.

$\left. \begin{array}{l} 1059 \cdot 8 \\ 1087 \\ 1133 \end{array} \right\}$ LEAD.

Very intense.

$\left. \begin{array}{l} 1221 \\ 1229 \end{array} \right\}$ Feebler group.
       Approximate wave-length.

THALLIUM.

1150.   Approximate wave-length.

BISMUTH.

$\left. \begin{array}{l} 837 \\ 973 \end{array} \right\}$ Approximate wave-lengths.

SILVER.

$\left. \begin{array}{l} 771 \\ 825 \end{array} \right\}$ Visible to the naked eye.

$\left. \begin{array}{l} 1083 \\ 1199 \end{array} \right\}$ TIN.

Nickel gave several rather feeble bands or groups of lines; whilst iron, in our experiments, gave no band sufficiently intense to examine.

The results, indicated above, show how rich the field of research is which the phenomena of phosphorescence open up in the invisible part of the infra-red of the spectrum, and which, alone, covers an interval of wave-lengths greater than the visible and ultra-violet parts together.

Besides the interest it may excite by proving the existence of these rays, of which the wave-lengths are considerable, in the spectra of metallic vapours, this research, more than any other, is of the kind to give most valuable information concerning the unknown laws which govern the vibratory motion of incandescent vapours.—*Comptes Rendus*, August 25, 1884.

CHANGE IN THE PHYSICAL PROPERTIES OF BISMUTH WHEN PLACED IN A MAGNETIC FIELD. BY M. HURION.

Recent experiments of M. Ledru (*Journal de Physique*, 2ᵉ série, vol. iii. p. 133), which may be easily repeated, show that if a plate of bismuth is placed in a magnetic field and at right angles to the lines of magnetic force, the equipotential surfaces of a current traversing the plate are deflected from their proper direction, from which it follows that the physical constitution of the metal is altered. This alteration may be revealed by other effects, especially by the action of polarized light.

Dr. Kerr's researches (Phil. Mag. May 1877) have shown that a mirror placed between the poles of an electromagnet rotates the plane of polarization of an incident perpendicular ray through a certain angle when the electromagnet is excited; the rotation is in the opposite direction of the current which produces the magnetization. Bismuth has similar properties, as follows from the following experiments.

A mirror is prepared whose reflecting surface is produced by running out the melted metal on a plate of glass heated, as done by M. Righi (*Journal de Physique*, 2ᵉ série, vol. iii. p. 127); the glass plate with a thin layer of metal is placed between the poles of a Faraday's electromagnet. The armatures of the electromagnet have a perforation in the centre; one of them is flat and the other conical, and the light comes through the aperture in the latter. The ray reflected at right angles returns in its original direction, and meets under an angle of 45° an uncoated glass which allows the direct light to pass, and directs the reflected ray sideways. The incident light traverses the polarizing system of a Laurent's saccharimeter, and the reflected light is received in an analyzer of the same material. The electromagnet may be traversed first in one direction and then in another by the current of a Gramme machine of the workshop type.

It is observed that the plane of polarization of the reflected ray is deflected by about 30' when the direction of the current is reversed; the rotation is in the same direction as the current which

produces the magnetization. It is clear that the effect observed is in part due to the action of the glass plate.

To allow for this latter action the bismuth may be removed from a small portion of the glass plate, and placing the analyzer at the other end of the apparatus we may examine the transmitted ray. It is found that the plane of polarization of the light which has passed through the glass turns through 24′ when the direction of the current is changed; the rotation, as is known, is in the direction of the current. But in the first experiment the glass plate, having been twice traversed by light, should have produced a rotation of 48′; observation gave 30′. We should conclude from this that bismuth has turned the plane of polarization through 18′ in the opposite direction of the current which excites the electromagnet. We may compare this result with the effect produced by a steel mirror placed under the same conditions; experiment shows a rotation of 22′ in the opposite direction of the current which excites the electromagnet.

If we cover again the steel mirror of the plate which carried the bismuth mirror, we observe a rotation of 28′ in the direction of the current, from which we may conclude that we shall have the special effect of the glass plate by adding to this rotation that produced directly by the steel, which gives for the effect of the plate 50′ instead of 48′, the number found above; the verification is therefore satisfactory. Experiments at present being made have shown me that the electrical resistance of bismuth increases when it is placed in a magnetic field.—*Journal de Physique*, August 1884.

ON THE DISTANCE OF THE POLES OF MAGNETS.
BY W. HALLOCK AND F. KOHLRAUSCH.

Most measurements of bar-magnets, of terrestrial magnetism, and galvanism, in so far as the distribution of the magnetism in a bar comes into account, may be arranged in such a way that, for ordinary purposes, we need go no further than for the knowledge of the position of the " poles." By this we understand here those points in which, in actions at a distance, we may assume the free magnetism, provided that the fourth power of the ratio of the length of the magnet to the distance from the magnet vanishes in comparison with unity. Ordinary long magnets have this property.

The distance of these poles from each other usually occur in corrections, which are sufficiently near if the polar distance is known to within a few percents. The question how far this is given by the form of the magnet plays an important part in electrical and magnetic measurements, for it influences their simplicity and, under some circumstances, even their accuracy.

One of us some time ago had endeavoured, by measurements with the tangent-galvanometer made in the Physical Institute in Göttingen, to determine the distance of the poles, and in connexion with these experiments had caused M. Schneebeli* to make some

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* *Progr. der Eidger. Polytechnik in Zürich*, 1871, p. 15 of the separate impression.

observations on bars and on needles by this method and by the method of deflections. The results of these experiments exhibited a suprising agreement among the various magnets, although the number of experiments was not so great as to exclude an accident.

We have therefore made a larger series of experiments of this kind, the provisional results of which are here given.

In these experiments we used :—

(1) The deflection of a short needle by the magnet to be examined in the ordinary way.

(2) The simultaneous action of the magnet on two magnetometers, between which the bar was placed, from two different positions. This process is one of great accuracy, since the alterations in temperature of the bar are without influence, and since the variations in the vertical component of the earth's magnetism completely, and the horizontal at any rate partially, disappear.

(3) The simultaneous action of currents in concentric circles of different diameters on the needle to be investigated. If the diameter of the coils is inversely as their number in each case, this method may be made in a form which even exceeds in simplicity and accuracy the preceding ; and is quite independent of external disturbance.

The factor with which the external length of the magnet must be multiplied in order to obtain the distance of the poles, that is to say the ratio of the ideal or reduced to the actual length, may be briefly called the modulus of the polar distance, and may be denoted in the following by k.

Fourteen magnets were used, some of them in various conditions of hardness. Where nothing else is said, they are cylinders magnetized in the direction of the axis.

1. Six recently prepared small round bars of the hardness of glass, 50 centim. in length, 40 centim. in thickness, and 5 grammes in weight, some magnetized to saturation, and some intentionally only partially magnetized, so that the specific magnetism was between 6 and 24 C. G. units for 1 gramme of steel, gave the modulus

$$k = 0.82 \text{ to } 0.86.$$

(After tempering in the lead-bath, the numbers increased, in some cases partly to 0.90.)

2. Two larger, externally equal magnets, which had long been in use, and had been frequently magnetized, 786 grammes in weight, dimensions $44 \times 2.3 \times 1.0$ centim. and with the specific magnetism 39, gave the values

$$k = 0.82 \text{ and } 0.83.$$

3. A hard hollow cylinder, 15 centim. long, of 1.6 centim. external diameter, weighing 109 grammes, and with the specific magnetism 32, and which had been treated by Strouhal's method, having been boiled during 30 hours since magnetizing, gave

$$k = 0.85.$$

4. A hard, massive steel cylinder recently hardened and magnetized, 16 centim. long, 1.48 centim. thick, and of the specific

magnetism 26, had

$$k = 0.81.$$

5. Finally, two bars of the same hard steel, 1·03 centim. thick, 30 and 20 centim. in length, and weighing 200 and 133 grammes respectively, the corresponding magnetizations being 42 and 28, gave

$$k = 0.82.$$

If we compare with these twelve bars, which together gave numbers between 0·81 and 0·86, the values previously found by Schneebeli for two bars, 0·84 and 0·86, together with the numbers observed by me for two magnetic needles, and, finally, the values recently given by von Helmholtz[*], 0·84 and 0·86; if, further, we consider the comparatively great difficulties and sources of error of such measurements, without which the differences would be still less, we may maintain with some certainty that the value

$$k = 0.83, \text{ or } 5/6$$

is very near for ordinary long magnets.   In other words,
The effective poles of a magnet are about $\frac{1}{12}$ of the distance from the ends.

On this assumption, we need never fear any errors amounting to 5 per cent. of the length ; and hence in many magnetic measurements there is no necessity for a separate determination of the distance of the poles.

Riecke has observed[†] that that distribution of the magnetism in a bar which had resulted from the experiments of Van Rees leads to a modulus of the polar distance of a similar magnitude to the above.

From their importance as magnetic needles, especially in galvanometers, we have examined a *circular magnet* and a *ring-magnet*, and, as observed above, by the simultaneous action of circular currents of the same diameter. Calling d the external diameter of the disk or of the ring, we found that in the factor of reduction of the tangent-compass which contained the member $3/16\,\lambda^2/R^2$, λ is to be introduced as the " length of the needle."

For the circular disk (diameter = 2·2 centim., thickness 0·17 centim., mass = 4·6 grammes, and specific magnetism = 7),

$$\lambda = 0.80\ d\ ;$$

and for the ring (external diameter 2·3 centim., internal diameter 1·9 centim., thickness = 0·22 centim., mass = 2 grammes, specific magnetism = 14),

$$\lambda = 0.88\ d.$$

Until a sufficiently large number of round magnets shall have been investigated, these numbers may afford at any rate an approximation.—Wiedemann's *Annalen*, No. 7, 1884.

[*] Von Helmholtz, *Sitzungsber. der Berliner Academie*, 1883, p. 405. Compare also Töpler, *ibid.* p. 2040, who confirms the value 5/6.
[†] *Ibid.* p. 319.

XLIII. *On the Numerics of the Elements.*
By EDMUND J. MILLS, *D.Sc., F.R.S.*[*]

I EMPLOY Professor James Thomson's expression "nu-
meric" as an abbreviation of "numerical value." The
numeric of an element is the numerical value ascribed to its
symbol.

Ever since Döbereiner's time[†] the relations between the
numerics of the elements have been felt to be a fascinating
study; but it was not until the discovery by Newlands[‡] of
the periodic function, that a closer and really comprehensive
grasp of the subject was rendered possible. The theory of
the periodicity of compounds was subsequently developed by
myself[§], under the name of " Cumulative Resolution."

It has of late years been admitted that it would be desirable
to place the periodicity of the elements on a more definite
numerical basis, and to include in it, if possible, a much
closer approximation to actual numerics than it has hitherto
contained. Accordingly, in 1879, I drew up a list of mean
values of the numerics of the elements; there was but little
difficulty in finding that these constituted a succession of
geometric series. At this point the work was laid aside for
further consideration. The appearance, in 1882, of Clarke's
able and exhaustive summary of all the evidence relating to

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[*] Communicated by the Author.
[†] Pogg. *Ann.* xci. p. 301 (1829). For this reference I am indebted
to Professor Ferguson.
[‡] For an epitome of Newlands's work, see 'The Periodic Law' (London:
Spon, 1884).
[§] Phil. Mag. [5] iii. p. 498. For the periodicity of the infinite olefines
of boiling-point and melting-point, see Phil. Mag. [5] xvii. p. 173.

the numerics, and of a treatise by Meyer and Seubert upon the same subject in 1883, placed ampler data in my hands. These have enabled me to calculate with considerable accuracy the three constants required by the consecutive equations.

If approximate trials be made with sets of contiguous numerics, it will soon become evident that every numeric is of the form

$$y = K - B\beta^x,$$

K being some integral multiple of a number near to 15, B being also near to 15, β the geometric factor, and x the ordinal in the series. If K be taken as once, twice, thrice, &c. 15, we shall have a succession of groups of numerics, and, putting $K = p\,15$, p will indicate their period. Lastly, we can calculate the largest value of β which we may use in common for all the groups, so as to make them interdependent: this number will obviously be more accurately determined than the other constants. The mean result from 37 numerics, distributed in 9 groups, has been found to be $\beta = \cdot93727$; for this, without sensible error, we may write $\beta = \cdot9375 = 15/16$. It is probable that the equation

$$y = p\,15 - 15(\cdot9375)^x$$

includes the numerics of all known elements excepting hydrogen.

In the following comparison of theory with experiment, I have depended mainly on Clarke's values :—

Group I.

$$y = 15 - 15(\cdot9375)^x.$$

					$x.$	$y.$	y calc.
Li	.	.	.	.	10	7·01	7·13
Be	.	.	.	.	14	9·09	8·92
Bo	.	.	.	.	20	10·94	10·87
C	.	.	.	.	25	11·97	12·01
N	.	.	.	.	42	14·02	14·00

Group II.

$$y = 30 - 15(\cdot9375)^x.$$

					$x.$	$y.$	y calc.
O	.	.	.	.	1	15·96	15·94
F	.	.	.	.	5	18·98	19·14
Na	.	.	.	.	12	23·00	23·09
Mg	.	.	.	.	15	24·28	24·30
Al	.	.	.	.	25	27·01	27·01
Si	.	.	.	.	32	28·20	28·10

Group III.

$$y = 45 - 15(\cdot9375)^x.$$

	$x.$	$y.$	y calc.
P	1	30·96	30·94
S	2	31·98	31·82
Cl	7	35·37	35·45
K	14	39·02	38·92
Ca	17	39·90	39·99
Sc	42	43·98	44·00

Group IV.

$$y = 60 - 15(\cdot9375)^x.$$

	$x.$	$y.$	y calc.
Ti	6	49·85	49·82
V	8	51·26	51·05
Cr	10	52·01	52·13
Mn	17	54·97	54·99
Fe	20	55·91	55·87
Ni	31	57·93	57·97
Co	41	58·89	58·94

Group V.

$$y = 75 - 15(\cdot9375)^x.$$

	$x.$	$y.$	y calc.
Cu	4	63·17	63·41
Zn	6	64·90	64·82
Ga	17	69·90	69·99
As	∞	74·92	75·00

Group VI.

$$y = 90 - 15(\cdot9375)^x.$$

	$x.$	$y.$	y calc.
Sc	5	78·80	79·14
Br	6	79·77	79·82
Rb	18	85·25	85·31
Sr	27	87·37	87·37
Yt	41	88·90	88·94
Zr	49	89·37	89·36

Group VII.

$$y = 105 - 15(\cdot9375)^x.$$

	$x.$	$y.$	y calc.
No (Cm)	5	93·81	94·14
Mo	7	95·53	95·45
Rh	42	104·06	104·00
Ru	46	104·22	104·43

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Group VIII.

$$y = 120 - 15(\cdot 9375)^x.$$

	x.	y.	y calc.
Pd	1	105·74	105·94
Ag	3	107·68	107·64
Cd	9	111·84	111·61
In	13	113·40	113·52
[Tb, De . . .	14	114	113·92]
Sn	29	117·70	117·69
Sb	∞	119·96	120·00

Group IX.

$$y = 135 - 15(\cdot 9375)^x.$$

	x.	y.	y calc.
I	9	126·56	126·61
Te	12	127·91	128·09
Cs	28	132·58	132·54

Group X.

$$y = 150 - 15(\cdot 9375)^x.$$

	x.	y.	y calc.
Ba	2	136·76	136·82
La	5	139	139·14
Ce	9	141·6	141·61
Di	18	145·2	145·31

Group XI.

$$y = 165 - 15(\cdot 9375)^x.$$

	x.	y.	y calc.
Sm	1	150·7	150·94

Group XII.

$$y = 180 - 15(\cdot 9375)^x.$$

	x.	y.	y calc.
Er	1	165·89	165·94
Yb	12	173·01	173·09

Group XIII.

$$y = 195 - 15(\ 9375)^x.$$

	x.	y.	y calc.
Ta	2	182·14	181·82
W	4	183·61	183·41
Ir	28	192·65	192·54
Pt	50	194·42	194·40

Group XIV.

$$y = 210 - 15(\cdot 9375)^{x}.$$

					x.	y.	y calc.
Au	.	.	.	.	1	196·16	195·94
Os	.	.	.	.	?		
Hg	.	.	.	.	6	199·71	199·82
Tl	.	.	.	.	13	203·72	203·52
Pb	.	.	.	.	22	206·47	206·37
Bi	.	.	.	.	28	207·52	207·54

Group XV.

$$y = 225 - 15(\cdot 9375)^{x}.$$

					x.	y.	y calc.
Ng	.	.	.	.	14	218·93	218·92

Group XVI.

$$r = 240 - 15(\cdot 9375)^{x}.$$

					x.	y.	y calc.
Tho	.	.	.	.	10	232·37	232·13
U	.	.	.	.	∞	239·70	240·00

On the Specific Values of some Numerics.

Nitrogen.—The details of Stas' recent work have not yet reached me. His latest result is 14·053.

Magnesium.—If we reject Dumas' determination (Clarke, p. 107), the mean of the older results is 24·19. The mean of this and Marignac's (1884), Mg = 24·37, has been accepted.

Potassium.—Stas' new result is stated as 39·142.

Manganese.—The best of the older work, in my opinion, is that of Berzelius and Turner: mean 54·86. Marignac (1884) gives 55·07. The mean of these numbers has been accepted. Dewar and Scott (1883) obtained 55·04.

Chromium.—Baubigny (1884) finds a still nearer value, viz. 52·16.

Nickel and Cobalt.—In spite of the very great labour already expended on these numerics, they still remain open to question. I have given Clarke's averages, which have, as will be observed, a *place* in the theory.

Copper.—Ever since the publication of Wright and Menke's "Notes on Manganese Dioxide" [Chem. Soc. J. (trans.) 1880, p. 22], I have felt grave doubts as to the exactness of the composition of higher oxides. The numeric of copper has been decided by several series of analyses of the higher oxide, confirmed by electrolysis of the sulphate. Both of

these methods might well lead to too high a result. A numeric founded on analyses of cuprous chloride or bromide would be much more satisfactory, and might not improbably correspond to $x = 3$.

Zinc.—Marignac (1884), using a method of obviously approximate character, gives Zn = 65·31.

Yttrium.—Cleve s numeric (1882) has been taken.

Tellurium.—Wills's best result [Chem. Soc. Journ. (trans.) 1879, p. 704] agrees, as will be noticed, closely with calculation.

Lanthanum, Cerium, and *Didymium.*—Here I have followed Brauner (1883), who determined the relation between oxide and sulphate. Robinson (1884), who determined the chlorine in cerous chloride, makes Ce = 139·90. If, in this group, $x = 6$, $y = 139·82$. Further experiment is necessary to decide this numeric.

Samarium.—Brauner (1883).

Ytterbium.—Nilson (1880).

Norwegium.—Dahll (1879).

Thorium.—Nilson (1883).

Uranium.—Peligot (1846).

Remarks and Inferences.

A comparison of the theoretical with the experimental numerics shows an extremely close agreement between them. Such a comparison is most rigorous when it is made for the best known numerics, and for low values of x; here the error (if it be indeed all error) does not exceed a moderate amount in the second decimal place.

The numerics of the elements have not all been determined in the same way—as, for example, by estimation of chlorine in the chlorides; and, though different methods of obtaining the same numeric lead generally to nearly the same result, they seldom involve exactly the same result. Thus our existing records do not enable us to say that the weight of Na that combines with the weight of Cl is precisely identical with the weight that combines with Br; nor does it necessarily follow that any single method of determination is in effect the same thing for all numerics. It is, in short, open to any theorist to express a given "definite proportion" in the form $a + md$; a being the invariable definite proportion as at present conceived, d the vapour-density of a varied element combining with a constant element, and m a small factor to be calculated from the experimental data. Hence the "error" of the geometrical theory, small though it is, is not necessarily all error; and it

opens up an entirely new field for chemical calculators. Our only existing resource is an average, in each particular case, of all unobjectionable results. In the present memoir these averages have been further subjected to geometrical average; each one thus connecting the other by a method far more severe than that of arithmetical means.

As regards the very interesting and perennial discussion of Prout's law, it is clear that the numerics which I have calculated are completely opposed to a theory of whole numbers, or integral multiples, for the great majority of the elements. Such a law can only hold in the few cases where $x=0$ or ∞; and As, Sb, and U appear to be the only instances of it.

If we consider the expression for any numeric,

$$y = p \cdot 15 - 15(\cdot 9375)^x,$$

we shall observe that, while the periodic factor continues to increase, the geometric portion of the equation undergoes no change. If p grew very large, a time would arrive when $-15(\cdot 9375)^x$ would cease to materially affect the value of $p\,15$. It is therefore easy to conceive the existence of an upper limit to our existing system of numerics; indeed, in the natural order of events, such a limit might occur without making p very large.

Chemists can hardly fail to be struck with the fact that $U = 240$ has for eight-and-thirty years of vigorous scientific research remained the highest value on their list. Another very interesting and tempting suggestion is latent in the series $15(\cdot 9375)^x$ itself. The sum of all its terms between 0 and ∞ is exactly 240; in other words, this number represents the total formative change in any given group. Hence 240 can hardly fail to be a critical number in, and may very probably be the upper limit of, our existing system.

If we accept this suggestion, the general equation for numerics assumes the following very simple character—

$$y = pn - n\left(\frac{n}{n+1}\right)^x,$$

$n+1$ being the number of groups in the system. Hydrogen, which all systematists agree in excluding from the common system, may from the new point of view be regarded as a relic of earlier changes embodied in the equation

$$y = 1 \times 1 - 1\left(\frac{1}{1+1}\right)^x.$$

This system would contain only two groups, of the first of which hydrogen would be the terminal member.

Glasgow, Oct. 10, 1884.

XLIV. *On* Laplace's *Equation. By* John H. Jellett,
D.D., Provost of Trinity College, Dublin[*].

THE equation upon which Laplace founded his discussion
of the problem of attraction has excited, as is well known,
a large amount of controversy.   No doubt, indeed, appears to
exist as to the truth of this equation in the case to which alone
Laplace has applied it, nor therefore as to the validity of the
method which he has built upon this foundation.   But Laplace
professes to demonstrate the truth of his equation for a case
more general than that which he subsequently considers; and
it is in this more general form that its truth has been ques-
tioned.   My object in the present paper is to endeavour to
determine exactly the limits within which Laplace's equation
is true, as it appears to me that these limits are somewhat
wider than has been generally supposed[†].

I proceed, in the first place, to give a proof of this equation
agreeing substantially with that given by Laplace, and then to
consider what conditions or limitations, if any, are necessary to
the validity of this proof.   Laplace's equation is as follows:—

Suppose the force of attraction to vary as the nth power of
the distance.   Let V be the potential of the attraction of a
nearly spherical body on a point upon its surface.   Let V_1 be
the potential (at the same point) of a sphere, touching the sur-
face at the point in question, and separated from it throughout
by a small distance, which we may denote by αu, α being a
small constant quantity, and u a function of the polar angles
θ, ϕ.   Let A, A_1 be the attractions, resolved along the common
normal, of the original solid and the sphere respectively.   Let
also b be the radius of the sphere.   Laplace's equation is
(*Méc. Cél.* Livr. 3, chap. ii. sect. 10),

$$V = V_1 + \frac{2b}{n+1}(A - A_1). \quad . \quad . \quad . \quad . \quad (1)$$

This equation may be put under a form somewhat simpler,
and which will enable us to mark more distinctly the limits
within which it is true.   Let v be the potential, at the point
of contact, of the shell included between the original surface
and the sphere.   Let also a be its normal attraction at the
same point.   Then

$$v = V - V_1, \quad a = A - A_1,$$

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[*] Communicated by the Author.
[†] "It may be taken, I think, as universally admitted that the equation
cannot be considered established if n is negative and numerically greater
than 2" (Todhunter, 'History of the Mathematical Theories of Attrac-
tion and the Figure of the Earth,' vol. ii. p. 263).

and the equation becomes

$$(n+1)v = 2ba ; \quad \ldots \quad \ldots \quad (2)$$

or, as it may be otherwise written,

$$(n+1)v = 2b\frac{dv}{dr}, \quad \ldots \quad \ldots \quad (3)$$

where r is the distance from the centre of the sphere of a point situated on the radius through the point of contact.

To prove this, Laplace assumes in the first place that the thin shell lying between the sphere and the original surface may be replaced by a "distribution" of matter (to use Gauss's expression) on the spherical surface itself. This assumption is only approximately true, inasmuch as it neglects the differences of distance among the particles situated on the same radius vector. The degree of the approximation will be considered further on.

Let P be the point of contact, and Q any other point on the surface of the sphere. Taking the origin, O, at the centre of the sphere, put $P \, O \, Q = \theta$, $PQ = \rho$, and let ϵ be the density of the distribution at the point Q. Then evidently

$$(n+1)v = b^2 \int_0^\pi \int_0^{2\pi} \epsilon \rho^{n+1} \sin\theta \, d\theta \, d\phi, \quad \ldots \quad (4)$$

$$a = b^2 \int_0^\pi \int_0^{2\pi} \epsilon \rho^n \cos \text{QPO} \sin\theta \, d\theta \, d\phi.$$

But

$$2 \text{OP} \cos \text{QPO} = 2 \text{PQ} = \rho,$$

whence

$$2ba = b^2 \int_0^\pi \int_0^{2\pi} \epsilon \rho^{n+1} \sin\theta \, d\theta \, d\phi. \quad \ldots \quad (5)$$

Hence $(n+1)v = 2ba$; and Laplace's equation is proved, if the foregoing integration be legitimate. It is of course only approximately true, the degree of approximation being the same as that of the assumption made in the beginning, namely that a distribution on the spherical surface may be substituted for the thin shell.

We have then to inquire, in the first place, what conditions are necessary to the validity of the integration indicated in (4) and (5), and, secondly, to what degree of approximation is the result true.

In reply to the first question, it may be said that it is sufficient to ensure the validity of the process of integration that the function to be integrated remain finite within the limits of integration. Thus, if the integral be $\int\int U \, d\theta \, d\phi$, it is

sufficient that U remain finite for all values of θ and ϕ included within the limits of integration. Applying this principle to the integral in (4) and (5), we see that the process of integration will be legitimate if $\epsilon \rho^{n+1} \sin \theta$ remain finite within the limits of integration. Now it is evident that this expression can become very great only when $n+1$ is negative and $\rho (= PQ)$ is very small. But if ρ is small, it is plain that θ is small. It will be sufficient, therefore, to consider the limiting value of $\epsilon \rho^{n+1} \sin \theta$ for very small values of θ. Now ϵ, the density of distribution, is proportional to the thickness of the shell at each point. Hence if a line be drawn from O, the centre of the sphere, cutting the sphere and the original surface in Q, Q' respectively, the density of distribution, ϵ, at the point Q, will be proportional to QQ'. Now, observing that OP is a normal to both surfaces, we see that, if $POQ (= \theta)$ be a small angle, QQ' cannot be of an order lower than θ^2. For both OQ and OQ' differ from OP by a quantity of this order. Hence the greatest value which ϵ can have at the point Q is $K\theta^2$, where K is finite. Again, $\rho = 2b \sin \frac{1}{2}\theta = b\theta$ nearly, and $\sin \theta = \theta$, to the same order. Hence $\epsilon \rho^{n+1} \sin \theta = K\theta^{n+4} +$ higher terms. It is evident, then, that $\epsilon \rho^{n+1} \sin \theta$ will not be infinite for $\theta = 0$ unless $n+4 < 0$. Laplace's equation is therefore true for all positive values of n, and for all negative values (except $n = -1$) which are not numerically greater than 4. The equation may be true for higher negative values of n than -4, if the sphere have contact of an order higher than the first with the original surface.

It remains to determine the degree of approximation to which the equation (2) is true. The order of the error in this equation is the same as that of the assumption by which this result was obtained, namely that a distribution on the surface of the sphere may be substituted for the shell.

Suppose that, in general, the potential of the shell is represented by the integral

$$\iiint f(r) \, dr \sin \theta \, d\theta \, d\phi.$$

Let

$$\int f(r) dr = f_1(r).$$

Then, the limiting values of r being $r = b$, $r = b + \alpha u$, the potential will be

$$v = \int_0^\pi \int_0^{2\pi} \{ f_1(b + \alpha u) - f_1(b) \} \sin \theta \, d\theta \, d\phi$$

$$= \int_0^\pi \int_0^{2\pi} \{ \alpha u f'b + \tfrac{1}{2} \alpha^2 u^2 f'(b) + \&c. \} \sin \theta \, d\theta \, d\phi.$$

If this expression be restricted to the first power of αu, the expression thus limited, namely

$$\int_0^\pi \int_0^{2\pi} \alpha u f(b) \sin\theta \, d\theta \, d\phi, \quad . \quad . \quad . \quad . \quad (6)$$

represents the potential of a superficial distribution whose density is αu. This is the form adopted by Laplace. The error in his result is therefore of an order not lower than α^2, provided that no one of the terms $u^2 f'(b) \sin\theta$, $u^3 f''(b) \sin\theta$, &c. become infinite within the limits of integration.

In the present case

$$f(r) = r^2 (r^2 + b^2 - 2br \cos\theta)^{\frac{n+1}{2}} = r^2 \{ (r - b\cos\theta)^2 + b^2 \sin^2\theta \}^{\frac{n+1}{2}}.$$

Assume $x = r - b\cos\theta$, $y = b\sin\theta$, $z = x^2 + y^2$. Then

$$f(r) = r^2 z^m, \text{ putting } m = \frac{n+1}{2}.$$

We have then to inquire whether any term such as

$$u^{p+1} \frac{d^p . r^2 z^m}{dr^p} \sin\theta$$

becomes infinite when $r = b$. But as neither r^2 or its differential coefficients can become infinite, it will be sufficient to determine the conditions necessary in order that

$$u^{p+1} \frac{d^p z^m}{dr^p} \sin\theta$$

may remain finite when $r = b$, and therefore $\theta = 0$. Now, since

$$\frac{dz}{dr} = 2x \frac{dx}{dr} = 2x,$$

we have

$$\frac{d^p z^m}{dr} = A z^{m-q} + B z^{m-q-1} x^2 + C z^{m-q-2} x^4 + \&c.,$$

or

$$= A' z^{m-q-1} x + B' z^{m-q-2} x^3 + \&c.,$$

according as $p = 2q$ or $= 2q + 1$. In both these series, since z and x are both of the order θ^2, when θ is small, it is easily seen that the first term is the term of the lowest order in θ. Moreover, as $u = 0$ and $\frac{du}{d\theta} = 0$ when $\theta = 0$, it is plain that u is also of the order θ^2 when θ is small. Hence when $p = 2q$, the order of the term $u^{p+1} \frac{d^p z^m}{dr^p} \sin\theta$ is

$$4q + 2 + 2m - 2q + 1 = 2q + 2m + 3 = 2q + n + 4 \, ;$$

and when $p = 2q + 1$, the order is

$$4q + 4 + 2(m - q - 1) + 2 + 1 = 2q + 2m + 5 = 2q + n + 6.$$

The term retained in the value of v, (6), corresponds to $p = 0$. The order of this term is therefore $=$ order of $\alpha + n + 4$, when θ is small. Hence if $n + 4$ be not < 0, the order of this term must be $=$ or $>$ order of α. The order of the next term will $=$ order of $\alpha^2 + n + 6$, and the orders of all succeeding terms will be higher when θ is small. The degree of the approximation is therefore as has been stated.

The same reasoning which has been applied to the potential will hold also for the resolved attraction. In fact, as we have seen, when θ is small the orders of the corresponding parts of the potential and of the resolved attraction are the same. Hence :—

If quantities proportional to the square and higher powers of the thickness of the shell be neglected, Laplace's *equation is true for all positive values of* n, *and for all negative values which do not numerically exceed* 4.

It will be observed that in the foregoing investigation I have taken Laplace's equation to refer, not to the potentials and attractions of the solids, but to the potential and attraction of the shell included between them. It is upon this consideration that the validity of the proof of Laplace's equation depends for negative values of n numerically greater than 2 and not numerically greater than 4. For such values of n the differential expressions for the attraction and the potential admit of a true integration for the shell, or its equivalent the material distribution. But these expressions do not necessarily in such cases admit of a true integration for either of the solids. Thus, if n be numerically greater than 2 and not greater than 3, the differential expression for the attraction does not admit of a true integration ; and if n be greater than 3, neither expression admits of a true integration. In the former case the attraction is infinite, and in the latter both attraction and potential are infinite.

Hence it is evident that the true cause of the failure of Laplace's equation (when it *does* fail) is that the quantities with which it is concerned cease to be finite. It does not fail for such a shell as Laplace describes, because the thickness of this shell is zero at the attracted point and exceedingly small in the immediate neighbourhood. It results from this construction of the attracting shell, that the potential and resolved attraction remain finite for higher inverse laws of force than they would for an ordinary solid.

XLV. *On the Specific Gravity of certain Substances in the Solid State and in Aqueous Solution.* By **J. A. Groshans**[*].

USEFUL compilations, like those of Landolt and Börnstein[†], render easy the observation of certain physical properties characterizing whole classes of bodies. We have been studying the specific gravities of some solid substances, and we will proceed directly to the discussion of one or two particular cases.

Analogous Compounds of Potassium and Sodium.

The atomic weight of sodium is 23 and its specific gravity 0·97; the atomic weight of potassium is 39 and its specific gravity 0·87 : sodium is the heavier of the two.

We find an apparent anomaly in all the compounds of these two bodies : in the solid state the sodium compound possesses a greater specific weight than that of the analogous compound of potassium, the two specific gravities bearing to one another the mean ratio of about 1·10 to 1. But for aqueous solutions, with an equal number of molecules of water (for example 100 and 200), the reverse is true ; for then the density of the solution which contains the potassium is always greater than the one containing the sodium. Table A shows the first case.

TABLE A.

The Specific Gravities, at the ordinary temperature, of the analogous compounds of Potassium and Sodium.

Example.	Potassium compound.	Specific gravity.	Sodium compound.	Specific gravity.	Ratio of specific gravities.
1	K Cl	1·977	NaCl	2·150	1·087
2	KBr	2·690	NaBr	3·014	1·120
3	KI	3·070	NaI	3·550	1·165
4	KF	2·481	NaF	2·766	1·115
5	KNO_3	2·092	$NaNO_3$	2·130	1·197
6	$KClO_3$	2·331	$NaClO_3$	2·289	0·982
7	$KBrO_3$	3·240	$NaBrO_3$	3·339	1·030
8	KIO_3	3·890	$NaIO_3$	4·277	1·100
9	KPO_3	2·258	$NaPO_3$	2·476	1·211
10	KOH	2·044	NaOH	2·130	1·042
11	K_2S	2·130	Na_2S	2·471	1·079
12	K_2CO_3	2·290	Na_2CO_3	2·476	1·081
13	K_2SO_4	2·647	Na_2SO_4	2·655	1·003
				Mean ratio	1·095

* Communicated by the Author, and translated from the French by Frederick H. Hatch.

† *Physikalisch-chemische Tabellen* (Berlin, 1883).

These data are taken from the tables of Landolt and Börnstein.

The second table, B, shows what we may call (in a certain sense) the opposite phenomenon. This table gives the densities of solutions containing one molecule of the soluble body with whole numbers (equal for the two bodies) of molecules of water; one sees clearly that the solutions which contain potassium are heavier than those containing sodium.

TABLE B.

Solutions of analogous compounds of Potassium and Sodium, containing one molecule of the soluble substance with n molecules of water, H_2O.

n H_2O.	Potassium compound.	Observed density.	Sodium compound.	Observed density.	Difference.
Thomsen's experiments . . $t=18°$.				
100	KCl	1·0258	NaCl	1·0234	0·0024
200	,,	1·0136	,,	1·0118	0·0018
200	KBr	1·0236	NaBr	missing	
200	KI	1·0335	NaI	1·0318	0·0017
100	KNO_3	1·0336	$NaNO_3$	1·0311	0·0025
200	,,	1·0173	,,	1·0160	0·0013
100	KOH	1·0284	NaOH	1·0246	0·0038
200	,,	1·0144	,,	1·0124	0·0020
100	K_2CO_3	missing	Na_2CO_3	1·0593	
200	,,	,,	,,	1·0306	
200	K_2SO_4	1·0380	Na_2SO_4	1·0350	0·0030
Nicol's experiments . . $t=20°$.				
100	KCl	1·0257	NaCl	1·0226	0·0031
200	,,	1·0131	,,	1·0115	0·0016
50	KNO_3	1·0652	$NaNO_3$	1·0598	0·0054
100	$KClO_3$	1·0412	$NaClO_3$	1·0384	0·0028
200	K_2SO_4	1·0376	Na_2SO_4	1·0347	0·0029
Gerlach's experiments . . $t=15°$.				
50	K_2CO_3	1·1249	Na_2CO_3	1·1114	0·0135
100	,,	1·0654	,,	1·0586	0·0068
200	,,	1·0334	,,	1·0301	0·0033
Kremers's experiments . . $t=19°·5$.				
100	KBr	1·0453	NaBr	1·0428	0·0025
200	,,	1·0230	,,	1·0216	0·0014

All the densities given in Table B are $d\,\dfrac{t^{\circ}}{t^{\circ}}$, and not $d\,\dfrac{t^{\circ}}{4^{\circ}}$. Those given under the names of Gerlach and Kremers are not the direct results of observation, like those of Thomsen and Nicol. We have calculated them from other experiments of the two observers; and we shall return later on to this calculation. These densities have been added to the table to fill up gaps in Thomsen's experiments. We have nothing to add concerning the compounds of potassium and sodium ; we therefore pass on to an analogous case.

Analogous Compounds of Fluorine and Chlorine.

It may have already been remarked, in Table A, how great the specific gravities of KF and NaF are, compared with the analogous compounds KCl and NaCl. In reality this case bears a strong resemblance to the one we have just been examining. The compounds of fluorine, of which the molecular weights are smaller than those of the analogous compounds of chlorine, have greater specific gravities ; the difference in the molecular weights $Cl-F$ is nearly equal to that between $K-Na$; being for $Cl-F=16\cdot5$ for one molecule, 33 for two molecules, and $49\cdot5$ for three molecules. However, the specific gravities of the fluorine compounds are greater than those of the chlorine compounds ; and the difference is about three times more than in our first case : this will be evident on referring to Table C.

TABLE C.

Specific Gravities, at the ordinary temperature, of the analogous compounds of Fluorine and Chlorine.

Example.	Fluorine compound.	Specific gravity.	Chlorine compound.	Specific gravity.	Ratio of specific gravities.
1	LiF	2·60	LiCl	2·04	1·275
2	NaF	2·77	NaCl	2·15	1·289
3	KF	2·48	KCl	1·98	1·253
4	MgF_2	2·47	$MgCl_2$	2·18	1·133
5	CaF_2	3·18	$CaCl_2$	2·22	1·433
6	BaF_2	4·83	$BaCl_2$	3·85	1·254
7	PbF_2	8·24	$PbCl_2$	5·80	1·421
8	AsF_3	2·67	$AsCl_3$	2·20	1·284
Mean ratio					1·293

The two compounds of arsenic, AsF_3 and $AsCl_3$, are, as we know, liquid at the ordinary temperature.

It may be asked, in what way does the phenomenon present itself in solutions ; which of the two solutions has the greater

density, that with F or that with Cl? For this we have not such a large number of examples as in the first case; we know that the greater part of the compounds of fluorine in Table C are insoluble.

We have come across Kohlrausch's researches on the fluoride of potassium, KF; and we have calculated, in round numbers, from his experiments the densities for integral numbers of molecules of water. The results of these calculations are in Table D; and we have placed opposite to them the observed densities of the solutions of KCl of Thomsen, with the same number of molecules of water.

<div align="center">Table D.</div>

Comparison of the Densities of Solutions of KF and KCl containing an equal number of molecules of water (n).

n. H_2O.	KF, Kohlrausch, $t=18°$. Calculated density.	KCl, Thomsen, $t=18°$. Observed density.	Differences.
15	1·1560	1·1468	0·0092
30	1·0832	1·0800	0·0032
50	1·0515	1·0496	0·0019
100	1·0263	1·0258	0·0005
200	1·0133	1·0136	0·0003

The densities here are $d\,\dfrac{t°}{t°}$.

We see in this table that the two solutions have equal densities when they are sufficiently dilute.

This example proves that the densities of solutions does not depend upon the greatness of the molecular weight of the dissolved substance; for the molecular weight of KCl is greater than that of KF.

On the Method employed in calculating the Densities of a Solution, with arbitrary numbers of Molecules of Water, taking two experiments for the basis of the Calculation.

In explaining this method of calculation, it will be necessary for us to touch upon some of the results of our researches upon solution, which have been published elsewhere.

We may regard a solution as a compound of one part (a gramme) of the soluble substance with a variable number of grammes of water; this number we will call aq. We shall show that the density of a solution can be represented with a

considerable degree of accuracy by the formula

$$d = 1 + \frac{\alpha}{\text{aq} + \beta}$$

(α and β are two constants given by two experiments).

Table E shows the agreement of the results obtained by the use of the interpolation-formula with the results of direct experiment. This table is copied from a publication of a research by Dr. G. Th. Gerlach[*].

TABLE E.

Experiments of Gerlach on a Solution of Crystallized Citric Acid; $t = 15°$.

Weight p in 100 parts of the dissolved body.	Aq. $\dfrac{100-p}{p}$.	$d\,\dfrac{15°}{15°}$ (observed).	Density (calculated).	Difference between calculated and observed result.
10	9	1·03916		
20	4	1·08052	1·080569	0·00005
30	2⅓	1·12439	1·124467	0·00008
40	1·5	1·17093	1·170950	0·00003
50	1	1·22041		

We see that the results obtained by use of the interpolation-formula leave nothing to be desired. The three results of the formula in the table have been calculated from two experiments, the first and the fifth, which give:—

$$\alpha = 0·380966 \qquad \log \alpha = 9·5807654$$
$$\beta = 0·72844$$
$$\overline{}$$
$$\alpha + \beta = 1·10941$$

The sum $(\alpha + \beta)$ has some importance. Suppose that a weighed quantity, say 10 grammes, of pure water, of which the volume at $4° = 10$ cubic centimetres and at $t°$ a little more, is added to a concentrated solution. Theoretically three cases can occur:—

1. The increase of volume of the solution can be exactly equal to the added volume of the pure water: in this case we should have $(\alpha + \beta) = 1$.

2. The increase of volume can be less than the added water; this is the ordinary case. It is then said that the solution is accompanied by "contraction;" in this case we find $(\alpha + \beta)$ greater than 1; in general the sum $(\alpha + \beta)$ is between 1 and 2.

3. In the third case the volume of the solution is increased

[*] *Specifische Gewichte der gebräuchlichsten Salzlösungen* (Freiberg, 1859).

by a greater quantity than the water which has been added ; $(\alpha + \beta)$ would be less than unity.

Space does not allow of our saying more about the sum $(\alpha + \beta)$.

Instead of considering solution as a combination of one gramme of the soluble body with aq grammes of water, one often prefers to consider it as a diffusion of a molecule part of the soluble substance, or a grammes (a being the molecular weight of the substance in solution) through n molecules of water ; instead of n we will employ the letter A. In this case we can make use of the same interpolation-formula, after having modified it in the following manner :—

Since $A = a/18$ aq., we multiply both terms α and β by $a/18$; the fraction remains unchanged ; and the new interpolation-formula becomes

$$d = 1 + \frac{\nu}{A + \lambda};$$

in which $\nu = a/18\,\alpha$, and $\lambda = a/18\,\beta$.

$$(\nu + \lambda)18/a = \alpha + \beta.$$

With this formula we have calculated the density of the solution of sugar, $C_{12}H_{22}O_{11}$, $a = 342$, according to the experiments of Gerlach. For the integral values (in round numbers) of A, we have taken, as the basis of our calculations, the two following experiments of Gerlach :—

Percentage p of sugar.	aq.	A.	Densities $17°·5/17°·5.$
5	19	361	1·019686
40	1·5	28·5	1·179358

From which we have

$$\nu = 7\cdot3526 \qquad \log \nu = 0\cdot8664411$$
$$\lambda = 12\cdot494$$
$$\nu + \lambda = 19\cdot8466 \qquad \alpha + \beta = 1\cdot043$$

Table F.

Solution of Sugar ; Gerlach's experiments at $17^c\cdot5$, and Marignac's at $20°$.

Molecules of H_2O. A.	Gerlach, calculated density. $d\frac{17°·5}{17°·5}$.	Marignac, observed density. $d\frac{20°}{20°}$.	Difference. G − M.
25	1·19610	1·19448	+0·00162
50	1·11765	1·11699	0·00066
100	1·06536	1·06517	0·00019
200	1·03460	1·03444	0·00016
400	1·01782	1·01770	0·00012

Table F contains the results of our calculations. We have chosen the same numbers for A that Marignac employed in his experiments upon the solution of sugar: and we have placed in the table the direct results of his observations, for the purpose of comparison. We see that the results of the two investigators, Gerlach and Marignac, very nearly agree. Gerlach's figures are a little high; but this little difference may be attributed to the difference of temperatures t°, which were 17°·5 C. for Gerlach and 20° C. for Marignac. We have still to multiply all the densities observed by Marignac by the number 1·001731, because he has expressed them with water at 4° C. taken as unity; his densities $d\dfrac{20^\circ}{4}$ have then been converted into $d\dfrac{20^\circ}{20^\circ}$, to render them, as nearly as possible, comparable with Gerlach's densities, 17°·51/17°·5.

The two interpolation-formulæ are not applicable to the densities $d\dfrac{t^\circ}{4^\circ}$. See Table G. In this table we have applied our formula to two of Marignac's series of densities, the densities 20°/4° and the densities 20°/20°.

Table G.

Marignac's experiments on Solutions of Sugar. Application of the Interpolation-formulæ to $d\,20^\circ/4^\circ$ and to $d\,20^\circ/20^\circ$.

A.	$d\,20^\circ/4^\circ$ (observed).	Density calculated by the formula.	Difference between observed and calculated density.
25	1·19242		
50	1·11506	1·11071	0·00435
100	1·06333	1·05986	0·00347
200	1·03265	1·03120	0·00145
400	1·01594		

A.	$d\dfrac{20^\circ}{4^\circ}$, converted to $d\,20^\circ/20^\circ$.	Density calculated by the formula.	Difference between observed and calculated density.
25	1·19448		
50	1·11699	1·11674	0·00025
100	1·06517	1·06488	0·00029
200	1·03444	1·03435	0·00008
400	1·01770		

For $d\ 20°/4°$ and $d\ 20°/20°$ the densities (in Table G) have been calculated three times from the first and fifth experiments. Using the densities $20°/20°$, we have

$$\nu = 7{\cdot}30208 \qquad \log \nu = 0{\cdot}8634464,$$
$$\lambda = 12{\cdot}5467$$

$$\text{Sum}\ldots\ 19{\cdot}8487 \qquad \alpha + \beta = 1{\cdot}0447.$$

These figures are almost the same as those which were obtained from Gerlach's two experiments.

Table G shows that the interpolation-formula represents, within a near approximation, the densities $20°/20°$—that is to say, the densities $t°/t°$; but not so well the densities $20°/4°$, or $d\ t°/4°$.

It would seem as if the density $t°/t°$ were the expression most suited to the nature of solution ; the conversion of $d\ t°/t°$ into $d\ t°/4°$ might resemble somewhat an arbitrary change, altering the nature of the results. At the same time, the densities $t°/t°$ have the advantage of making it easier to compare the results of different observers. This would still more be possible if all investigators were to make use of the same fixed temperature $t°$ when the so-called ordinary temperature is in question.

We could also wish that it were always clearly stated if the temperature in question be $t°/t°$ or $t°/4°$; one is often in doubt about this important point, especially when obliged to cite from second-hand sources. But we must proceed.

We have shown the method we have employed in Kohlrausch's experiments on the solution of KF, which are described in the important work of G. Wiedemann on Electricity, vol. i. p. 593. In all, we have chosen three experiments.

Kohlrausch's experiments on a solution of KF.

p.	aq.	A.	$d\ 18°/18°$.	$d\ 18°/4°$?
5	19	$61\frac{2}{9}$	$1{\cdot}0424$	$1{\cdot}041$
10	9	29	$1{\cdot}0854$	$1{\cdot}084$
40	1·5	4·833	$1{\cdot}3798$	$1{\cdot}378$

We have commenced by changing the given densities (those with three decimals), which we suppose to be $18°/4°$, into $18°/18°$. We have then calculated the two constants, taking the mean of the first and third experiments ; and have thus obtained the following mean result:—

$$\nu = 2{\cdot}69133 \qquad \log \nu = 0{\cdot}4299663$$
$$\lambda = 2{\cdot}25270$$

$$\text{Sum} \ldots 4{\cdot}94403 \qquad \alpha + \beta = 1{\cdot}5343$$

Applying the formula thus obtained to the second experiment, we have :—

$$d\ 18°/18°\text{ (observed)} = 1\cdot0854$$
$$d\ 18°/18°\text{ (calculated)} = 1\cdot0861$$

If a similar calculation be made for KCl from Thomsen's two experiments (given in Table D) corresponding with A = 15 and 100, the following results are obtained :—

$$\nu = 2\cdot6606 \qquad \log \nu = 0\cdot4249793$$
$$\lambda = 3\cdot1240$$

Sum ... $5\cdot7846$ $\qquad \alpha + \beta = 1\cdot397$

We see that the two solutions (that of KF and that of KCl) have almost the same ν ; but the two λ's are a little different:

$$\text{For KCl, } \lambda = 3\cdot124$$
$$\text{,, KF, } \lambda = 2\cdot253$$

$$\text{Difference} = 0\cdot871$$

This difference, which is somewhat large, varies with the different densities of the two substances in the solid and anhydrous state (see Table C).

We may here mention a special property of our interpolation-formula.

If aq or A be made $= 0$, the formulæ become

$$d = 1 + \frac{\alpha}{\beta} = 1 + \frac{\nu}{\lambda} = \delta;$$

and they then express the specific gravity of the dissolved substance in the anhydrous state ; we call this particular value of d, δ.

The value of δ, calculated by the formula, in some cases approaches very nearly to that of direct observation. For example, Marignac gives somewhere the specific gravity of crystallized sugar as $1\cdot59$.

Now our calculations (from $d\ 20°/20°$) give

$$\delta = 1 + \frac{\nu}{\lambda} = 1\cdot582.$$

Since, according to Table C, the specific weights δ, observed for KF and KCl, are respectively $2\cdot48$ and $1\cdot98$, and thus far from equal, it follows that in the two substances we may have $\nu = \nu'$ (nearly), but not $\lambda = \lambda'$; for (assuming our interpolation-formula and the results of observation to be perfectly accurate) we should have for

KF. $\qquad\qquad$ KCl.
$$\delta = 1 + \frac{\nu}{\lambda} = 2\cdot48; \quad \delta' = 1 + \frac{\nu'}{\lambda'} = 1\cdot98.$$

Whereas, starting from the values of ν and λ, which have been obtained by calculation (by means of two experiments for each substance), we have :—

For KF, $\delta = 2.19$; for KCl, $\delta = 1.85$.

These figures do not agree so well as those for the sugar ; but the agreement appears to us sufficient.

We see, in using this form of the interpolation-formula

$$d = 1 + \frac{\nu}{A + \lambda},$$

that when two different substances have the same ν (which often occurs), but slightly different values of λ, the densities of the two solutions can differ slightly for small values of A; but that the difference diminishes for greater values of A, and that the two densities become equal when $A = \infty$. This result for KF and KCl may be seen in Table D.

There are some substances which not only have the same ν but also the same λ, which occurs (ν, ν' being assumed equal) when two similar substances have the same specific gravity in the anhydrous state. We will give a single example of this.

On referring to Landolt's tables, we find for the two following substances :—

		Mean.
PbN_2O_6......	$\delta = 4.34$ to 4.58	4.46
SrI_2	δ to $10°$	4.41

We have calculated ν and λ for these substances according to the following experiments of Kremers :—

Kremers's experiments.

	SrI_2.			PbN_2O_6.	
$p.$	Water.	$d\ 19°.5/19°.5.$	$p.$	Water.	$d\ 19°.5/19°.5.$
27.5	100	1.2160	11.10	100	1.0931
127.9	100	1.8349	59.02	100	1.4496

$$\nu = 15.7803 \qquad \nu = 15.793$$
$$\lambda = 4.0673 \qquad \lambda = 3.970$$

Sum ... 19.8476   Sum ... 19.763

$$\alpha + \beta = 1.046, \qquad \alpha + \beta = 1.0747.$$
$$\delta \text{ calc.} = 4.88, \qquad \delta \text{ calc.} = 4.98.$$

Similar solutions of the two substances with an equal number,

A, of molecules of water have necessarily equal densities. We shall be pardoned the following calculations :—

Densities 19°·5/19°·5, calculated from Kremers's experiments.

A.	SrI_2.	PbN_2O_6.
50	1·2919	1·2926
100	1·1516	1·1519
200	1·0773	1·0774
300	1·0391	1·0391

Among Thomsen's experiments the following is to be found:—

$$PbN_2O_6 + 200H_2O, \ d\,18°/18° = 1·0771.$$
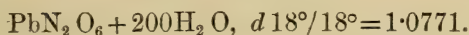
Conclusion.

It is possible to form groups of substances of which the densities are equal when $A = A'$. For instance, this is the case for the homonymous salts of Fe, Mn, and Cr. We call the following salts homonymous:—

$$RSO_4; \quad RCl_2; \quad RN_2O_6; \quad \&c.$$
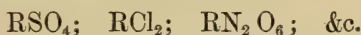
The same holds good for the homonymous salts of Cu, Zn, Ni, and Co.

The following Table H contains several experiments (which have already been published) referring to this last case.

TABLE H.

Solutions with Equal Densities.

Thomsen's experiments. $t = 18°$.			
A	Dissolved substance.	$d\,t°/t°$.	Mean.
200	$ZnSO_4$	1·0455	1·0449
200	$CuSO_4$	1·0444	
Nicol's experiments.			
207	$ZnSO_4$	1·04367	
207	$CuSO_4$	1·04268	
207	$CoSO_4$	1·04304	1·04308
207	$NiSO_4$	1·04296	

For two substances which possess the same ν the values of α, α' are inversely proportional to the molecular weights a, a'.

It is often possible to foretell the value of ν which a substance will have, by making use of certain observations on the properties of solutions. For instance, if two substances be taken, RI_2 and RBr_2, R being the same for both, it will be found for the two substances,

$$\nu - \nu' = \text{constant.}$$

We may express this result in a more general manner, thus:—

$$I - Br = \text{constant.}$$

In the same way,

$$Br - Cl = \text{constant.}$$

And, further, these two constants are equal to one another; so that we have

$$I - Br = Br - Cl = \text{constant.}$$

When two substances, such as RI_2 and $R'I_2$, have R, R' different, *e. g.* Zn and Mg, we find in all cases, such as ZnI_2 and $Mg\,I_2$, or $ZnSO_4$ and $MgSO_4$, &c.,

$$Zn - Mg = \text{constant.}$$

The metals Ca, Sr, Ba give (like Cl, Br, I):—

$$Ba - Sr = Sr - Ca = \text{constant.}$$

Space does not permit of our continuing this subject, which we have treated elsewhere in several published papers.

Scheveningen, Holland,
    August 1884.

XLVI. *An overlooked Discoverer in the Theory of Determinants.* By Thomas Muir, *M.A., LL.D., F.R.S.E.*[*]

1. NOTWITHSTANDING the care which has been taken, especially on the Continent, in investigating the history of the Theory of Determinants, and notwithstanding the fact that, practically, the history extends no further back than somewhere about 130 years, there seems to be at least one investigator of considerable importance who has been altogether lost sight of. This is Ferdinand Schweins, born at Fürstenberg, Paderborn, in 1780, Professor in Heidelberg from 1811, died in 1856. Some time ago I came into possession of his *Theorie der Differenzen und Differentiale*, a handsome quarto volume of vi + 666 pages, published in 1825. On reading the title-page, which enumerates six other subjects besides Differences and Differentials, I found the names of two

of them unfamiliar, viz. " gedoppelte Verbindungen " and " Producte mit Versetzungen," and turned over the necessary pages to see what exactly these terms were used to denote. To my astonishment, " Producte mit Versetzungen " proved to be nothing more nor less than Determinants ; and I soon saw that what I had been fortunate enough to light on was a very complete treatise on the subject, extending to 113 pages.

The historical interest attaching to this work of Schweins would alone render it desirable that some account of the contents should be published; but an additional inducement exists in the fact that some of the results are not without a savour of freshness even at the present day.

2. The *Theorie der Producte mit Versetzungen* begins at p. 317. There is an introduction of four pages, in which the author refers in the first place to mathematicians who had previously dealt with the subject, and then indicates, in the form almost of a table of contents, the nature and extent of his own investigations. The names he mentions are those of Euler, Cramer, Bézout, Hindenburg, Rothe, Laplace, Desnanot, and Wronski. One of these, Desnanot, it may be remarked, is even now new to us in connexion with the history of Determinants. As for their influence upon Schweins, it may be said in a general way that, while he belonged to the Combinatorial School of Hindenburg, it seems to have been the writings of Wronski that in the main directed and inspired his efforts.

What is not a little remarkable is the omission of Cauchy's name, the one really great name that could have been referred to in connexion with the subject. Cauchy's memoir (*Sur les fonctions* &c.) appeared in the year 1812 ; so that, so far as date of publication is concerned, it would seem to have stood as good a chance of being known as either the work of Wronski (1811 &c.) or of Desnanot (1819). Its existence undoubtedly lessens the importance to be attached to Schweins' work.

3. The *Theorie* consists of four sections (*Abtheilungen*), subdivided into portions which we may call Chapters. The first Section has *five* chapters; the second also *five* ; the third, *one* ; and the fourth, *four*.

Sect. I. Chap. 1.

On the Nature of "Producte mit Versetzungen."

4. The " elements " from which the products are formed are denoted thus :—

$$\overset{a_1}{A_1}, \quad \overset{a_2}{A_1}, \ldots$$

symbols for which we now should use

$$A_{1, a_1}, \quad A_{1, a_2};$$

the letter A being accompanied by two suffixed numbers, the second of which is itself a letter with a suffix.

A determinant with elements of this kind is denoted by the principal term enclosed within the brackets

$$\| \quad);$$

thus

$$\| \overset{a_1}{A_1} \overset{a_2}{A_2}) \equiv \overset{a_1}{A_1} \overset{a_2}{A_2} - \overset{a_2}{A_1} \overset{a_1}{A_2}.$$

This notation, and no other, is used throughout the whole treatise. As the name " Producte mit Versetzungen " implies, the view taken of a determinant is as an aggregate of terms one of which gives rise to all the others by permutation of suffixes : naturally, therefore, determinants with elements other than those specified above do not occur, and "rows" and " columns " are things unthought of.

The definition adopted is a statement of the recurring law of formation—that is to say, the law of development of a determinant of the nth order in terms of determinants of the $(n-1)$th order ; a definition, by the way, recently employed by Professor Cayley in his article on Determinants in the *Encyclopædia Britannica*.

Immediately following the definition are given careful enunciations and proofs of the following theorems:—

I. The suffixes being allowed to remain unchanged, the superfixes (*die oberen Elemente*) are interchanged in every possible way to obtain the full development.

II. The sign preceding each term is dependent upon the number of interchanges of places necessary to arrive at the term.

III. If two adjacent superfixes be interchanged, the sign of the determinant is altered.

IV. If a superfix be moved a number of places to the right or left, the sign of the determinant is changed or not according as the number of places is odd or even.

V. If several superfixes change places, the sign of the determinant is altered or not according as the number is odd or even which indicates how often a smaller superfix follows a greater.

VI. If in any *term* the number which indicates how often a smaller superfix follows a greater be even, the sign preceding the term must be positive, and if the number be odd the sign must be negative.

VII. Instead of keeping the suffixes unchanged and inter-

changing the superfixes when finding the development, we may do the opposite with the same effect: and theorems III. to VI. hold when " suffix " is put for " superfix."

VIII. (Development of a determinant in terms of binary products of a row and column.)

This is given incidentally, but is quite generally stated and proved.

IX. (Development of a determinant in terms of products of complementary minors.)

This also is enunciated and proved in all its generality.

X. If two suffixes or superfixes be identical, the determinant vanishes.

XI. If the first element of a row of a determinant be multiplied by the cofactor of the first element of another row, the second element of the former row be multiplied by the cofactor of the second element of the latter, and so on, the sum of the products is equal to zero.

Of these theorems only two, those here marked IX. and X., are claimed by Schweins as his own. This of course they really are not; X. having been enunciated by Vandermonde, and IX. being due in some considerable part to Vandermonde and Laplace. To Schweins, however, belongs distinctly the credit of the formal and general enunciation of the latter theorem, and a systematic proof of it.

But although the individual results of the chapter were not new when published, the chapter viewed as a whole (that is to say, as an orderly arranged and rigidly demonstrated body of truth) was undoubtedly " a new thing."

Sect. I. Chap. 2.

5. The title of this chapter is not sufficiently definite; it should be *Transformation of a series whose terms are products of pairs of determinants into another similar series.*

The first identity which is given showing such a transformation is in modern notation,

$$| a_1 b_2 c_3 d_4 | | e_5 f_6 g_7 | - | a_1 b_2 c_3 e_4 | | d_5 f_6 g_7 |$$
$$+ | a_1 b_2 c_3 f_4 | | d_5 e_6 g_7 | - | a_1 b_2 c_3 g_4 | | d_5 e_6 f_7 |$$
$$= | a_1 b_2 c_3 | | d_4 e_5 f_6 g_7 | - | a_1 b_2 c_4 | | d_3 e_5 f_6 g_7 |$$
$$+ | a_1 b_3 c_4 | | d_2 e_5 f_6 g_7 | - | a_2 b_3 c_4 | | d_1 e_5 f_6 g_7 |.$$

This Schweins establishes by expanding the first factor of each product on the left-hand side in terms of the elements of its last row and their complementary minors, and then, by means of the same theorem, combining in new sets of four the

sixteen terms thus obtained. In fact the sixteen terms may be written in order in four rows of four each; and these being viewed as four *columns* of four each, and the columns summed, we obtain the right-hand member of the identity.

It is then shown that this is a case of a general theorem in which the factors of each product are determinants of the $(n+1)$th and mth orders, the said theorem being accurately and succinctly stated by means of a suitable notation.

Even here, however, the matter does not end; for by a quite natural step Schweins passes on to a much more widely general theorem, in which the factors on the one side are determinants of the $(p+s+q)$th and $(k+p)$th orders, while those on the other are determinants of the $(p+s)$th and $(q+k+p)$th orders.

The conclusion of the chapter is occupied with the statement of a considerable number of interesting special cases of the latter theorem.

6. There can be no doubt that almost every detail of this chapter was new at the time of publication; and it is therefore of some importance that the nature of its contents be properly understood. This will be most readily attained if we present them shortly in the light in which nowadays they would naturally be viewed.

In the case of the special identity with which the chapter opens, a writer of the present time would only require to direct attention to the determinant

$$\begin{vmatrix} a_1 & a_2 & a_3 & a_4 & \cdot & \cdot & \cdot \\ b_1 & b_2 & b_3 & b_4 & \cdot & \cdot & \cdot \\ c_1 & c_2 & c_3 & c_4 & \cdot & \cdot & \cdot \\ d_1 & d_2 & d_3 & d_4 & d_5 & d_6 & d_7 \\ e_1 & e_2 & e_3 & e_4 & e_5 & e_6 & e_7 \\ f_1 & f_2 & f_3 & f_4 & f_5 & f_6 & f_7 \\ g_1 & g_2 & g_3 & g_4 & g_5 & g_6 & g_7 \end{vmatrix}$$

whose non-zero elements form a quadrate gnomon of the dimensions 4, 7, 4; and point out that this determinant is the natural sum, according to Laplace's expansion-theorem, of the left-hand member of the identity, and likewise of the right-hand member; the former being obtained by developing the determinant in terms of the minors of the 4th order got from the first four columns, and the latter by developing it in the same way in terms of the minors of the 4th order got from the last four rows.

Then from the gnomon (4, 7, 4) he would pass to the gnomon (p, n, q), n being unequal to $p+q$, and finding, as before, its two developments in terms of complementary minors with non-zero elements, would at once arrive at Schweins' most general theorem.

7. The essence of the chapter would thus be seen to be *the equating of the two possible developments of a quadrate gnomon in terms of products of complementary minors with non-zero elements* ; and if we should wish to attach to the theorem a depreciatory technical label, we might characterize it as but the statement of the "*dimorphic expansibility of a quadrate gnomon.*"

The very reverse of depreciation must, however, be our feeling when we recall the date 1825 ; and when we bear in mind the fact that a formal statement of the general identities, independent of the way in which they may be established, has not even yet found its way into our textbooks, such modern mathematicians as Sylvester (1851) having enunciated only special cases, and the masterly memoir of Reiss (1867) having been as nearly as possible altogether neglected.

8. The following is Schweins' statement of the most general of the theorems :—

$$\Sigma \pm \left| \begin{array}{c} a_1 \cdots\cdots\cdots\cdots\cdots a_n \\ A_1 \ldots A_{n-q} \ \ B'_1 \ldots B'_q \end{array} \right| \cdot \left| \begin{array}{c} b_1 \cdots\cdots b_{(m-q)} \\ B'_{q+1} \ldots B'_m \end{array} \right|$$

$$= \Sigma \pm \left| \begin{array}{c} a'_1 \cdots\cdots\cdots\cdots\cdots a'_{(n-q)} \\ A_1 \ldots\cdots\cdots\cdots\cdots A_{n-q} \end{array} \right| \left| \begin{array}{c} a'_{(n-q+1)} \ldots a'_n, b_1 \ldots b_{(m-q)} \\ B_1 \ldots\cdots\cdots\cdots B_m \end{array} \right|.$$

The only points about it requiring explanation are the exact effect to be given to the symbol Σ and the meaning of the dashes affixed to certain of the letters. The two symbols are connected with each other, the dashes not being permanently attached to the letters, but merely put in to assist in explaining the duty of the Σ. On the left-hand member of the identity the two symbols indicate that the first term is got by dropping the dashes, and that from this first term another term is got if we substitute for $B_1 \ldots B_q$ some other set of q B's chosen from $B_1 \ldots B_m$, and take the remaining B's to form the B's of the second determinant, the two sets of B's being in both cases first arranged in ascending order of their suffixes. On the other side of the identity the use of the symbols is exactly similar, $n-q$ of the n superfixes $a_1, \ldots, a_n$ being taken for the first determinant of any term of the series and the remainder for the second determinant. The number of terms in the series on the one side is evidently $m!/q!(m-q)!$, and on the other $n!/q!(n-q)!$

Thus in the case where $n=4$, $q=2$, $m=5$ the identity is written

$$\Sigma \pm \left| \begin{matrix} a_1 & a_2 & a_3 & a_4 \\ A_1 & A_2 & B'_1 & B'_2 \end{matrix} \right| \left| \begin{matrix} b_1 & b_2 & b_3 \\ B'_3 & B'_4 & B'_5 \end{matrix} \right|$$

$$= \Sigma \pm \left| \begin{matrix} a'_1 & a'_2 \\ A_1 & A_2 \end{matrix} \right| \cdot \left| \begin{matrix} a'_3 & a'_4 & b_1 & b_2 & b_3 \\ B_1 & B_2 & B_3 & B_4 & B_5 \end{matrix} \right| ;$$

and this is meant to indicate that

$$\left| \begin{matrix} a_1 & a_2 & a_3 & a_4 \\ A_1 & A_2 & B_1 & B_2 \end{matrix} \right| \left| \begin{matrix} b_1 & b_2 & b_3 \\ B_3 & B_4 & B_5 \end{matrix} \right| - \left| \begin{matrix} a_1 & a_2 & a_3 & a_4 \\ A_1 & A_2 & B_1 & B_3 \end{matrix} \right| \left| \begin{matrix} b_1 & b_2 & b_3 \\ B_2 & B_4 & B_5 \end{matrix} \right|$$
$$+ \ldots (10 \text{ terms})$$

$$= \left| \begin{matrix} a_1 & a_2 \\ A_1 & A_2 \end{matrix} \right| \left| \begin{matrix} a_3 & a_4 & b_1 & b_2 & b_3 \\ B_1 & B_2 & B_3 & B_4 & B_5 \end{matrix} \right| - \left| \begin{matrix} a_1 & a_3 \\ A_1 & A_2 \end{matrix} \right| \left| \begin{matrix} a_2 & a_4 & b_1 & b_2 & b_3 \\ B_1 & B_2 & B_3 & B_4 & B_5 \end{matrix} \right|$$
$$+ \ldots (6 \text{ terms}),$$

where the suffixes of the B's in the first factors of the terms on the left-hand side are in order

$$12, 13, 14, 15, 23, 24, 25, 34, 35, 45,$$

and the sign of any term is determined by the number of inversions of order among the suffixes of *all* the B's mentioned in the term; while the suffixes of the a's in the first factors of the terms on the right-hand side are

$$12, 13, 14, 23, 24, 34;$$

and the sign of any term is determined by the number of inversions of order among the suffixes of all the a's of the term.

9. The notation which in our time would almost certainly be chosen for the statement of such identities is the umbral notation of Sylvester. In outward appearance it is not unlike that of Schweins, although in essence it is different. The superfixes of Schweins are, like the suffixes, appendages of the capital letters A and B; whereas with Sylvester, and indeed also with Leibnitz and Vandermonde, the capital letters are dispensed with. Using then

$$\left| \begin{matrix} a & b & c \cdots \\ \alpha & \beta & \gamma \cdots \end{matrix} \right| \text{ for } | A_{a\alpha} \ A_{b\beta} \ A_{c\gamma} \cdots |,$$

and placing a line over or under the variables instead of marking them with a dash, we may write Schweins' identity thus:—

$$\Sigma \pm \left| \begin{matrix} a_1 \ldots a_{n-q} \overline{\ b_1 \ldots \ldots b_q\ } \\ \alpha_1 \ldots \ldots \ldots \ldots \ldots \alpha_n \end{matrix} \right| \cdot \left| \begin{matrix} b_{q+1} \ldots b_m \\ \beta_1 \ldots \beta_{m-q} \end{matrix} \right|$$

$$= \Sigma \pm \left| \begin{matrix} a_1 \ldots a_{n-q} \\ \underline{\alpha_1 \ldots \alpha_{n-q}} \end{matrix} \right| \cdot \left| \begin{matrix} b_1 \ldots \ldots b_q & b_{q+1} \ldots b_m \\ \alpha_{n-q+1} \ldots \alpha_n & \beta_1 \ldots \beta_{m-q} \end{matrix} \right|.$$

This could scarcely be improved upon. The letters on the one side are in order exactly the same as those on the other; the only difference, in fact, between the sides being in the position of three of the straight lines.

10. When in the generating gnomon one of the incomplete rows is identical with the corresponding part of one of the complete rows, or when more than one such pair of partially identical rows exist, a number of the products on the left-hand side vanish; and the theorem then becomes :—

$$\Sigma \pm \left| \begin{array}{cc} a_1 \ldots a_{p+s} & \overline{b_1 \ldots b_q} \\ \alpha_1 \ldots\ldots\ldots\ldots\ldots \alpha_{p+s+q} \end{array} \middle| \begin{array}{cc} b_{q+1} \ldots b_{q+k} \; a_1 \ldots a_p \\ \beta_1 \ldots\ldots\ldots\ldots\ldots \beta_p \end{array} \right|$$

$$= \Sigma \pm \left| \begin{array}{c} a_1 \ldots a_{p+s} \\ \alpha_1 \ldots \alpha_{p+s} \end{array} \middle| \begin{array}{cc} b_1 \ldots b_q & b_{q+1} \ldots b_{q+k} \; a_1 \ldots a_p \\ \alpha_{p+s+1} \ldots \alpha_{p+s+q} \; \beta_1 \ldots\ldots\ldots\ldots\ldots \beta_p \end{array} \right|.$$

This is the first special case which Schweins gives.

The next case is virtually the same, as his notation leads him to consider as different two theorems which are derivable the one from the other by the interchange of rows and columns.

The third case arises when in the generating gnomon there exist, in addition to the partially identical rows just referred to, one or more pairs of *columns* having the like partial identity : the theorem then is

$$\left| \begin{array}{cc} a_1 \ldots\ldots\ldots a_{p+s} \\ \beta_1 \ldots \beta_h \; \alpha_1 \ldots \alpha_{p+s-h} \end{array} \middle| \begin{array}{cc} b_1 \ldots\ldots\ldots b_q & b_{q+1} \ldots b_{h+k-p+q} \; a_1 \ldots a_p \\ \alpha_{p+s-h+1} \ldots \alpha_{p+s-h+q} \; \beta_1 \ldots\ldots\ldots\ldots\ldots \beta_{h+k} \end{array} \right|$$

$$\left| \begin{array}{cc} a_1 \ldots\ldots\ldots a_{p+s} & \overline{b_1 \ldots\ldots\ldots b_q} \\ \beta_1 \ldots \beta_h \; \alpha_1 \ldots \alpha_{p+s-h} \; \alpha_{p+s-h+1} \ldots \alpha_{p+s-h+q} \end{array} \middle| \begin{array}{cc} b_{q+1} \ldots b_{h+k-p+q} \; a_1 \ldots a_p \\ \beta_1 \ldots\ldots\ldots\ldots\ldots \beta_{h+k} \end{array} \right|.$$

The first two of these three special cases he then further specializes, putting in the first $k=0$, and in the result thence obtained $q=1$, and so on.

11. It is rather strange that Schweins did not observe what is perhaps the neatest, and certainly is now the best known special case of all, viz. that which is got from the general theorem by putting

$$\left. \begin{array}{l} m = q + n \\ \beta_1, \ldots, \beta_n = \alpha_1, \ldots, \alpha_n \end{array} \right\}.$$

and

In this case all the determinants on the right-hand side vanish, and the theorem takes the form

$$\Sigma \pm \left| \begin{array}{cc} a_1 \ldots a_{n-q} \; \overline{b_1 \ldots b_q} \\ \alpha_1 \ldots\ldots\ldots\ldots \alpha_n \end{array} \middle| \begin{array}{c} b_{q+1} \ldots b_{q+n} \\ \alpha_1 \ldots \alpha_n \end{array} \right| = 0,$$

which is the identity published by Sylvester in the Philosophical Magazine for August 1851 (ser. 4, vol. ii. pp. 142–145). In the statement of it there given one of the products is on the one side, and the rest on the other, some affected by the sign + and some by the sign −. A modification of this, which is simpler in that all the signs are positive, is given in my 'Theory of Determinants,' p. 124, viz.:—"*The product of two determinants of the same order is equal to the sum of like products obtained by interchanging* q *chosen columns of the one determinant with every set of* q *columns of the other in succession: the interchange of* q *columns with* q *columns being effected by interchanging the first column of the one set with the first column of the other, the second of the one with the second of the other, and so on.*"

12. The only mathematician whom Schweins mentions as having preceded him in handling such identities as are given in this chapter is Desnanot, to whom he attributes the very simple instances

$$\Sigma \pm \begin{vmatrix} a_1 & a_2 & \overline{b_1} \\ \alpha_1 & \alpha_2 & \alpha_3 \end{vmatrix} \begin{vmatrix} b_2 & b_3 & b_4 & b_4 \\ \alpha_1 & \alpha_2 & \alpha_3 & \alpha_4 \end{vmatrix} = 0,$$

$$\Sigma \pm \begin{vmatrix} a_1 & \overline{b_1} \\ \alpha_1 & \alpha_2 \end{vmatrix} \begin{vmatrix} b_2 & b_3 & b_4 \\ \alpha_1 & \alpha_2 & \alpha_3 \end{vmatrix} = 0.$$

It deserves, however, to be noted that Bézout was much more worthy of being mentioned. We find on pp. 185, 186, 187 of the *Théorie générale des Equations Algébriques*, published in 1779, the identities

$$|a_0 b_1| \, |c_0 d_1| - |a_0 c_1| \, |b_0 d_1| + |b_0 c_1| \, |a_0 d_1| = 0,$$

$$|a_0 b_1 c_2| \, |d_0 e_1| - |a_0 b_1 d_2| \, |c_0 e_1| + |a_0 c_1 d_2| \, |b_0 e_1| - |b_0 c_1 d_2| \, |a_0 e_1| = 0,$$

$$|a_0 b_1 c_2| \, |d_0 e_1 f_2| - |a_0 b_1 d_2| \, |c_0 e_1 f_2| + |a_0 c_1 d_2| \, |b_0 e_1 f_2| - |b_0 c_1 d_2| \, |a_0 e_1 f_2| = 0$$

the second of which is the same as the second of Desnanot's as given above, and the first and third are cases of Sylvester's Theorem. Besides it must be noted that these were viewed by their author as merely simple instances of an unlimited series of identities. His words are (p. 187, § 223):—

"*En voilà assez pour faire connoître la route qu'on doit tenir, pour trouver ces sortes de théorêmes. On voit qu'il y a une infinité d'autres combinaisons à faire, et qui donneront chacune de nouvelles fonctions, qui seront zéro par elles-mêmes: mais cela est facile à trouver actuellement.*"

There is thus no small share of credit to be assigned to Bézout. It is of no consequence as an objection to say that the identities are not given by Bézout in determinant

notation; for this also he could have done, as may be seen on looking at p. 211, &c., where he uses

(ab') for $ab' - a'b$,

$(ab'c'')$ for $(ab' - a'b)c'' - (ab'' - a''b)c' + (a'b'' - a''b')c$,

and so on. It was reserved for Professor Cayley, a hundred years after the date of Bézout's work, to point out that the "proper proof" of the identities is by means of what we have called the generating gnomon (Quart. Journ. of Math. xv. pp. 55–57).

Sect. I. Chap. 3.

13. The title of this chapter is "*Transformation of determinants into other determinants when the elements are connected by linear equations.*" What it really gives is the familiar solution of a set of simultaneous linear equations by means of determinants.

Sect I. Chap. 4.

14. The subject-matter here is a *special form* of determinant, viz. that in which each element is zero whose column-number exceeds its row-number by more than unity. The one theorem given is very interesting, and has not, I think, been published elsewhere up till now.

For the purpose of more readily giving expression to it, let us use the symbol

$$(a\ b\ c\ d\ e;\ f)_2$$

to stand for the sum of all the terms whose factors are f and *two* of the letters a, b, c, d, e; that is to say, for

$$abf + acf + adf + aef + bcf + bdf + bef + cdf + cef + def;$$

and, similarly,

$$(1;\ 2, 3, 4, 5, 6)_2$$

for

$$123 + 124 + 125 + 126 + 134 + 135 + 136 + 145 + 146 + 156;$$

and thus finally

$$\begin{pmatrix} a, & b, & c, & d, & e; & f \\ 1, & 2, & 3, & 4, & 5, & 6 \end{pmatrix}_2$$

for

$$a_1 b_2 f_3 + a_1 c_2 f_4 + a_1 d_2 f_5 + a_1 e_2 f_6 + b_1 c_3 f_4 + b_1 d_3 f_5 + b_1 e_3 f_6$$
$$+ c_1 d_4 f_5 + c_1 e_4 f_6 + d_1 e_5 f_6;$$

the combinations of a, b, c, d, e and of $1, 2, 3, 4, 5, 6$ taken two together being arranged in order. Further, let us specialize the form of the determinant somewhat more by making

all the elements 1 whose column-number exceeds the row-number by unity. This, of course, is a specialization more apparent than real. Then, for the case of the fifth order, the theorem is

$$
\begin{vmatrix}
a_1 & 1 \\
b_1 & b_2 & 1 \\
c_1 & c_2 & c_3 & 1 \\
d_1 & d_2 & d_3 & d_4 & 1 \\
e_1 & e_2 & e_3 & e_4 & e_5
\end{vmatrix}
= e_1 - \begin{pmatrix} a, & b, & c, & d; & e \\ 1; & 2, & 3, & 4, & 5 \end{pmatrix}_1 + \begin{pmatrix} a, & b, & c, & d; & e \\ 1; & 2, & 3, & 4, & 5 \end{pmatrix}_2
$$
$$
- \begin{pmatrix} a, & b, & c, & d; & e \\ 1; & 2, & 3, & 4, & 5 \end{pmatrix}_3 + a_1 b_2 c_3 d_4 e_5.
$$
$$
= \sum_{r=0}^{r=4} (-)^r \begin{pmatrix} a, & b, & c, & d; & e \\ 1; & 2, & 3, & 4, & 5 \end{pmatrix}_r ;
$$

and, quite generally,

$$
\begin{vmatrix}
\binom{1}{1} & 1 & 0 & 0 & \dots & 0 \\
\binom{2}{1} & \binom{2}{2} & 1 & 0 & \dots & 0 \\
\binom{3}{1} & \binom{3}{2} & \binom{3}{3} & 1 & \dots & 0 \\
. & . & . & . & . & . \\
\binom{n}{1} & \binom{n}{2} & \binom{n}{3} & \binom{n}{4} & \dots & \binom{n}{n}
\end{vmatrix}
= \sum_{r=0}^{r=n-1} (-1)^r \begin{pmatrix} 1 \dots n-1; & n \\ 1; & 2 \dots \dots n \end{pmatrix}_r,
$$

the number of terms on the right-hand side being evidently 2^n. The theorem enables one to write out the final development of a determinant of this kind *currente calamo*. Thus, to return to the above determinant of the fifth order, we have at once as its equivalent

$$
e_1 - (a_1 e_2 + b_1 e_3 + c_1 e_4 + d_1 e_5) + (a_1 b_2 e_3 + a_1 c_2 e_4 + a_1 d_2 e_5 + b_1 c_3 e_4
$$
$$
+ b_1 d_3 e_5 + c_1 d_4 e_5) - (a_1 b_2 c_3 e_4 + a_1 b_2 d_3 e_5 + a_1 c_2 d_4 e_5 + b_1 c_3 d_4 e_5)
$$
$$
+ a_1 b_2 c_3 d_4 e_5.
$$

Sect. I. Chap. 5.

This ostensibly concerns the quotient of a determinant of the order ∞ by another determinant of the same order, the determinants being different in only one of their rows. The following will suffice to show the nature of the single result which is obtained.

It is readily seen that, as a very special instance of the theorem of chap. 2,

$$
| a_1 b_2 c_3 d_4 | \, | a_1 c_2 d_3 e_4 f_5 | - | a_1 c_2 d_3 e_4 | \, | a_1 b_2 c_3 d_4 f_5 |
$$
$$
+ | a_1 c_2 d_3 f_4 | \, | a_1 b_2 c_3 d_4 e_5 | = 0.
$$

And hence on dividing by $|a_1 b_2 c_3 d_4||a_1 b_2 c_3 d_4 e_5|$, we have

$$\frac{|a_1 c_2 d_3 e_4 f_5|}{|a_1 b_2 c_3 d_4 e_5|} - \frac{|a_1 c_2 d_3 e_4||a_1 b_2 c_3 d_4 f_5|}{|a_1 b_2 c_3 d_4||a_1 b_2 c_3 d_4 e_5|} + \frac{|a_1 c_2 d_3 f_4|}{|a_1 b_2 c_3 d_4|} = 0.$$

Similarly,

$$-\frac{|a_1 c_2 d_3 f_4|}{|a_1 b_2 c_3 d_4|} + \frac{|a_1 c_2 d_3||a_1 b_2 c_3 f_4|}{|a_1 b_2 c_3||a_1 b_2 c_3 d_4|} - \frac{|a_1 c_2 f_3|}{|a_1 b_2 c_3|} = 0;$$

and

$$\frac{|a_1 c_2 f_3|}{|a_1 b_2 c_3|} - \frac{|a_1 c_2||a_1 b_2 f_3|}{|a_1 b_2||a_1 b_2 c_3|} + \frac{|a_1 f_2|}{|a_1 b_2|} = 0;$$

and therefore by addition,

$$\frac{|a_1 c_2 d_3 e_4 f_5|}{|a_1 b_2 c_3 d_4 e_5|} = \frac{|a_1 c_2 d_3 e_4||a_1 b_2 c_3 d_4 f_5|}{|a_1 b_2 c_3 d_4||a_1 b_2 c_3 d_4 e_5|} - \frac{|a_1 c_2 d_3||a_1 b_2 c_3 f_4|}{|a_1 b_2 c_3||a_1 b_2 c_3 d_4|}$$
$$+ \frac{|a_1 c_2||a_1 b_2 f_3|}{|a_1 b_2||a_1 b_2 c_3|} - \frac{|a_1 f_2|}{|a_1 b_2|}.$$

In the quotient on the left of this identity the determinants may evidently be of any higher order, the right-hand member having then a correspondingly greater number of terms. In Schweins' final result the said determinants are of the order ∞.

[To be continued.]

XLVII. *On the Conductivity of Tourmaline for Heat.* By Franz Strenger[*].

THEORETICAL considerations on the causes of pyroelectrical phenomena led S. P. Thompson and O. J. Lodge[†] to the supposition that tourmaline possesses a unilateral conductivity for heat in the direction of the principal axis, and that therefore the conductivity in the direction from the analogous pole to the antilogous pole is different from the conductivity in the reverse sense. To verify their assumption they made two different series of experiments. In one of these they used De Sénarmont's method:—Slices of the crystal, cut parallel to the axis, were covered with thin layers of wax, and the curves were then observed to which the wax melted when a point of the plate was warmed by applying a hot wire. They then found, as they had supposed, that the isothermal curves

† S. P. Thompson and O. J. Lodge, Phil. Mag. [5] viii. p. 18 (1879).

were not true ellipses, but appeared distorted in the direction from the heated point towards the analogous pole.

Such observations gave for the ratio between the semiaxes of the isothermal curves, along the principal axis, the mean value of 100 : 129.

In a second series of experiments, a tourmaline slice, cut at right angles to the crystallographic axis, was fixed between two glass tubes ; into the upper of these a weighed quantity of mercury was poured, while into the lower steam was blown. The time was observed which was required to raise the temperature of the mercury through a given number of degrees.

A difference in the conductivity, according to the direction in which the heat flowed through the tourmaline, was also observed by this method of experimenting. The mean values of the times required to produce an equal elevation of temperature bore to one another the ratio of 100 : 119.

The few measurements made by Thompson and Lodge differ so widely from one another, that the existence of a unilateral conductivity cannot be inferred with certainty from these experiments. Above all, it should first have been accurately ascertained that the slices used were perfectly homogeneous; that is, that the crystal was not made up of a number of crystalline individuals so grown together as to have the analogous and antilogous poles, of different crystals, lying beside one another in the same surface. It was therefore desirable to find a better method of experimenting, to decide whether tourmaline possesses this abnormal conductivity for heat or not.

The experiments made by me for this purpose were performed upon two slices cut at right angles to the principal axis. The one, about 5·8 millim. thick, was cut from a crystal from Brazil, belonging to the Mineralogical Institute of this University, and was placed at my disposal by Prof. Bücking; the other from a detrital peeble from Ceylon. Neither of them showed any trace of a fibrous structure ; and a careful pyro-electrical examination, according to Kundt's[*] method (which is founded on the principle of Lichtenberg's figures), showed that the two slices were in fact absolutely homogeneous; for the crystal having been heated, and, while cooling, dusted over with the proper mixture, showed one of the two surfaces perfectly yellow, the other perfectly red.

The method employed in experimenting on the conductivity for heat has been adapted from one used by F. Weber[†] for liquids. A thermoelectric junction, fixed in a copper cylinder,

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[*] Wied. *Ann.* xx. p. 592 (1883).

[†] F. Weber, Wied. *Ann.* x. p. 103 (1880).

rests on the tourmaline plate. Both the junction and the plate
are allowed to acquire the temperature of the room; the under
surface of the slice is then cooled to 0° C. by bringing it in
contact with a smooth surface of ice, and the change of tem-
perature is read off on the scale of a delicate mirror-galvano-
meter. The galvanometer (fig. 1, G) used by me was one of
small resistance, with an astatic needle and a powerful damper.

Fig. 1.
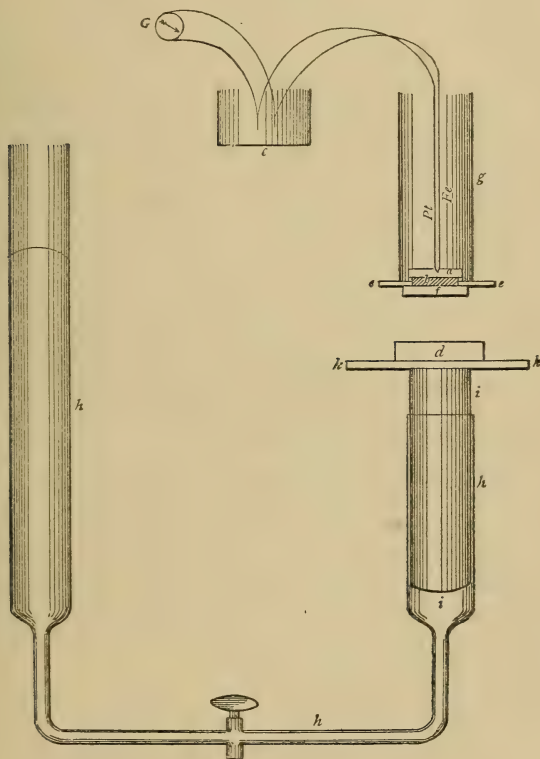
The one junction (*a*) of the thermoelectric element (a copper
cylinder about 4 millim. high, upon the surface of which a
platinum and an iron wire were soldered) rested, to insure
good contact, upon a small layer of mercury (*b*) on the tour-
maline plate (*f*); both junctions of the platinum and iron
wires with the galvanometer-wires dipped into a glass vessel
(*c*) containing oil of turpentine, which was placed in a wooden
box lined with cotton-wool in order to keep the temperature
as constant as possible. The temperatures were read off upon

a Geissler's thermometer, with which it was possible to read to the 100th of a degree.

In the beginning of an experiment, F. Weber caused the temperature of the lower surface of the substance to be examined to sink to 0° C., and to remain there by placing the crystal plate and the metal vessel containing the thermo-junction directly upon a smooth surface of ice. I could not adopt this method of proceeding ; for the weight of the tourmaline slice and the copper cylinder was too small to drive away the water, produced by the melting ice, and to preserve a good contact. I have therefore preferred to leave the tourmaline slice unchanged in its position, and, by a special arrangement, to approach the plane surface of the ice (d) from below, and to press it so tightly as to drive the water away from the neighbourhood of the tourmaline plate.

For this purpose the slice (f) was cemented, with a little wax and rosin, to an ebony plate (e), which was penetrated by a hole of the required size, and this again to a short glass tube (g); the glass tube was then clamped to a retort-stand.

Vertically under the plate was the shorter arm of a U-tube (h), which communicated with the other by means of a thinner tube provided with a stopcock. In the shorter arm was a test-tube, movable with little friction : upon the upper end of this, directly under the tourmaline itself, a glass plate (k) was cemented. The U-tube was filled with mercury until the glass plate was about 2 centim. under the surface of the crystal ; the stopcock was then closed, and the longer arm filled to the top with mercury. If it was now required to cool the lower surface of the tourmaline plate to 0° C., a piece of ice (about 1 centim. thick), possessing a plane surface, was placed upon the glass plate, and the cock opened; the mercury in the longer arm then raised the test-tube, and with it the ice, and pressed the latter firmly against the crystal.

In order to be able to compare the results of different experiments, I kept the temperature of the room as constant as possible ; if the temperature got too high in the course of the afternoon, I stopped the experiment and proceeded with it the next morning. Besides this, sufficient time was allowed, by every measurement, to enable the whole extent of the crystal to acquire the same temperature as the thermoelectric junction (a) and the air of the room.

Before and after every experiment, I made certain that no electromotive force could come into play other than that caused by the difference of temperature between the copper cylinder and the thermoelectric junction in the oil of turpentine. Lastly, the ice approached the tourmaline so rapidly that,

before the contact, no change of temperature of the junction (*a*) was observable.

The experiment was conducted in the following way :—I first observed the position of the needle at rest with a closed circuit ; I then short-circuited the current (excluding the three thermoelectric junctions) to convince myself of the absence of every other electromotive force ; the temperature of the turpentine was now read, and after removing the short circuit the deviation of the magnetic needle observed. The piece of ice was then placed on the glass plate of the test-tube, the stop-cock opened, and with the help of a chronometer the moment of contact between the ice and the tourmaline slice observed through a telescope. In order to keep the readings for the different times expressed in divisions of the scale, the junction (*a*) was then immediately placed in ice and the deviation noted. The results were controlled at the end of every experiment by observing whether the temperature of the turpentine and the deviation of the needle, by open and by short circuit, were the same as before.

In this way a number of experiments were made for both tourmaline slices, sometimes the analogous, sometimes the antilogous, end of the crystal being brought into contact with the ice. The results I represented graphically by means of curves, of which the number of seconds, reckoned from the first contact of the tourmaline with the ice, form the abscissæ, and the corresponding temperatures of the junction (*a*), expressed in scale-divisions, the ordinates. The galvanometer was so arranged that about sixty divisions on the scale corresponded to $1°$ C. difference of temperature.

Of the curves thus obtained only the middle one has been used. The first shows, naturally, a less regular course ; while the last is also useless, because the changes of temperature towards the end of the experiment took place rather slowly, making the errors of observation of course greater. For the thicker slice I have used, in the construction of the curve, the part between the abscissæ $t = 20$ seconds and $t_1 = 200$ seconds ; for the thinner, in which the rise of temperature takes place with more rapidity, from $t = 20$ to $t_1 = 150$ seconds.

In consequence of the unavoidable variations in the temperature of the room in which the observations were made, the first few ordinates of the temperature-curves obtained in the different experiments are not quite equal ; the greatest difference which I have allowed amounts to 3 per cent. In order to obtain from all the experiments the probable change of temperature for one and the same position of one of the slices, I have increased or diminished the curve in such a way that for

$t = 20$ seconds the ordinates of all the curves have one and the same value. For the later times the different curves will be

Fig. 2. Crystal from Brazil.
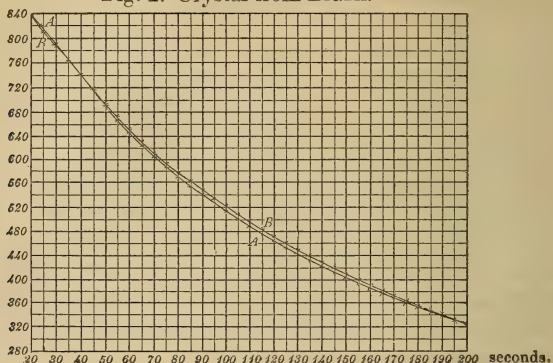
Fig. 3. Crystal from Ceylon.
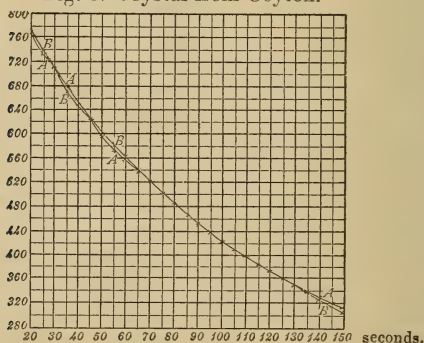
somewhat differently shaped ; and the most probable temperature-curve for any particular temperature at commencing will be obtained if, for its ordinates, the mean values of the ordinates of the new curves be chosen. This method of proceeding is not strictly correct. As, however, experiment shows that the different temperatures at commencing of corresponding curves approach one another more and more as one proceeds to greater abscissæ, and the variation among the individual curves being moreover small, the error can be of little importance.

Concerning the curves, which have been reduced so as to have the same temperature at commencing, I only repeat the statement that the deviations amount at most to 3 per cent. In figs. 2 and 3 I give the most probable temperature-curves, obtained in the way given above, for the two slices : here A denotes the line obtained when the flow of heat is from the analogous to the antilogous pole, and the corresponding one (B) in the reverse direction.

As may be seen, the curves A and B for both plates approach one another very nearly. The greatest difference between two corresponding ordinates is about 1 per cent., or not more than the differences which have occurred in experimenting with the slice in one position.

From this the inference may be drawn that a unilateral conductivity for heat is present in tourmaline either to a very small degree or, what seems more probable, not at all.

Phys. Inst. Univ. Strassburg,
        May 1884.

XLVIII. *On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling. By* JAMES HOPPS, *Superintendent of Workshops, Royal Indian Engineering College, Cooper's Hill**.

[Plate IX.]

DURING the past winter, while assisting a pupil to make some resistance-coils, I was struck with the great difference that often existed between the resistance of the wire before it was coiled on to its bobbin and after; the difference was not always constant or proportional to the length of the wires used, and appeared to be largely influenced by the tension with which the wires were coiled on to the bobbins.

Some of the coils altered so much after winding as to lead to the supposition of their being short-circuited; and on uncoiling several of these and recoiling at a lower tension, the resistance would alter considerably.

The diameter of the bobbin used also appeared to have great influence in producing changes in the resistance.

A great portion of the alterations appeared to be temporary.

As has been observed above, the differences were not always constant; neither were they regular in their signs, *i. e.* they would sometimes show an increase and sometimes a decrease of resistance, but generally the change would be one of increase.

Having resolved to make some efforts to clear up this matter, I first sought to find what had been done by others in this direction. A very careful search through books and also of the Transactions of the Royal Society afforded no evidence that this field had been even entered upon, *i. e.* any attempt by experiment or otherwise to determine and account for the effects of coiling and uncoiling on the electrical resistance of metallic wires.

After experimenting some weeks, I purposely attended the meeting of this Society on February 23rd to hear a paper,

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* Communicated by the Physical Society.

"On the Adjustment of Resistance-Coils," by Prof. Silvanus P. Thompson ; and although some of the difficulties in the way of adjusting resistance-coils were spoken of, yet the difficulty that had given us so much trouble was not once alluded to, either in the paper or in the discussion which followed. At the close of the proceedings, in the course of a short conversation with Prof. Thompson, and in reply to a question from myself, he stated that he had observed that the resistance of a wire was altered by being coiled. Mr. Latimer Clark also observed that he had noticed the change, but added that the changes were not always constant, giving sometimes an increase and sometimes a decrease in the resistance. Now experiments had given me the same results, and had the subject cropped up during the discussion, I had prepared a few notes to give to the meeting.

The fact of having obtained sometimes + and sometimes − readings had puzzled me much, but after the conversation above alluded to I resolved to continue my experiments; and although these are yet far from complete, I have felt it my duty to lay the results already obtained before the Society.

Before going into a description of the apparatus and method employed (part of the apparatus is before you), I would crave a few moments to allude to some of my earlier experiments. These were conducted in a very primitive way ; but the results obtained, although appearing so erratic and contradictory, have been in a great measure confirmed by using the more elaborate method employed later on. In confirmation of this I would draw your attention to the great resemblance which exists between the two curves on the diagram, which are the curves of copper wires produced by hand- and machine-winding respectively.

The method first employed to investigate this effect was to let the wire under test form one side of a Wheatstone bridge, doubling the wire into a loop as in a resistance-coil, and rolling it by hand on to a cylinder or other shapes in wood. The resistance could thus be taken after each operation without the necessity of altering the connexions.

The time lost in waiting until the heat imparted to the wire through handling had disappeared was great, and the uncertainty as to the tension with which the wire was coiled and uncoiled caused me to seek some other method.

After many schemes the one before you was adopted. Bearing in mind that many of the wires to be experimented upon would not be insulated, and would be of many different diameters and rigidities, it was very early evident that the drum on which the wires were to be coiled would also have to insulate each convolution from its neighbour as well as to wind up

the wire. The different diameters and rigidities also determined the necessity of being able to vary the tension. The insulation is obtained by using an ebonite drum to receive the wire; on this drum a right- and left-handed screw has been cut. The variation in the tension may be obtained in two different ways, or by a combination of both:—1st, by altering the load carried in the little waggon which runs up and down the inclined plane; 2nd, by altering the angle of inclination of the plane; or we may combine both if necessary.

As the application of longitudinal strain to a wire while being tested for resistance has been shown to be considerable, it was necessary to relieve the wire from the strain due to the load before taking the resistance, otherwise the changes due to strain would have been included in the readings. To remove the strain, the waggon on arriving at the bottom of the plane rests against a stop; on being drawn to the top the plane is brought to a position slightly above the horizontal; these allowing in both cases the drum to slightly unwind itself, and consequently the strain on the wire is almost entirely removed.

The ebonite drum, as before observed, has a right- and left-handed screw cut upon it; these meet in the middle of its length. A screw holding down an ebonite cap here passes through the inside of the loop of the wire under test, and fixes it firmly, but without injury, to the drum; the ends of the wire are carried up the plane to two binding-screws, and with the necessary leading wires form one side of a Wheatstone bridge.

A long length of stout whipcord is attached to the middle of a winding drum underneath the head of the plane, and the ends, after being coiled between the empty threads of the ebonite drum (starting from the centre), are fixed to the ends of the drum. On turning the drum below, the cords pull on the top part of the ebonite drum, causing it to revolve; and at the same time that the cord is being payed off, the wire under test is being coiled on in its place. This is continued until the waggon arrives at the top; a pawl working on a ratchet-wheel prevents the waggon running back until the plane has been brought to a horizontal position, where, after resting five minutes, the resistance is taken. The operations are now reversed; and after a similar rest at the bottom, the resistance is again taken. And these operations are repeated, each operation taking about six minutes, giving an average of ten per hour; they were generally continued for three hours, giving for each series about thirty readings, and then allowed to stand until the following evening, all strain being previously removed.

The temperature of the laboratory was carefully regulated each evening, for two hours before commencing work, to the

same temperature as on the previous evening, and kept constant within half a degree Fahr. $\pm$.

In the case of some wires as many as 380 readings have been taken altogether; this was on lead wire No. 5. At the end of the seventh series the wire broke.

The curves of resistance of four of the seven series of tests on this wire is very interesting. It will be observed that, while being very similar to each other, there is a point marked (a) on each series where coiling and uncoiling produce an increase in the resistance. Again, the wonderful power of recovery which is shown by the wire after each rest is very marked; the normal condition would appear to be to give positive and negative readings, and that this condition is upset after a time. The inability to recover this condition has suggested that, when this point has been arrived at, it might be said to represent the commencement of a kind of electrical fatigue.

There are some other points on this diagram, and which are more or less repeated by every other wire that I have tested, which furnish matter for speculation; such as—why should coiling generally produce a less effect than uncoiling? and why should the signs be generally different? and why should those signs in many cases become reversed?

An *increase* of resistance on uncoiling and a *decrease* on coiling take place with lead, copper, German silver, aluminium, and magnesium; and also with the first few operations on soft iron wire, after which the signs are completely changed.

An increase almost invariably follows coiling and uncoiling with zinc, but the effect of coiling varies from one half to one thirtieth of the effect of uncoiling.

The difference between coiling and uncoiling, or, we might say, the amplitude of the differences of resistances, is greatest in the case of magnesium and least in the case of aluminium; the latter, on referring to the curves, will be seen to alter very little indeed.

The amplitude of the differences in the case of hard-drawn German silver is not so great after a few series; and when annealed, after showing great increases after standing at rest, the final series approach very near to that of the hard-drawn wire, which is strong evidence indeed that the wire has become harder through repeated coiling and uncoiling.

The length of the wires were very carefully taken before and after the experiments, and the necessary calculations made for alterations in length and cross-section according to the formula $R \propto \dfrac{l}{a}$, in which R = the resistance, l = the length, and a = the area of the cross section.

After making these corrections, the changes in the resistance remaining unaccounted for are:—

Metals.	Of the increase on the original resistance.	Of the actual observed change.
Iron	2·3 per cent.	81·64 per cent.
Lead (average of six)	1·27 ,,	2·91 ,,
Copper	1·18 to 1·42 per cent.	57·58 to 60·7 per cent·
Zinc	1·23 to 2·16 ,,	23·6 to 42·4 ,,
Aluminium	0·77 to 2·206 ,,	41·15 to 72·01 ,,
German silver (annealed) ...	0·054 to 0·171 ,,	11·89 to 21·6 ,,
Magnesium No. 2..............	1·549 per cent.	

With magnesium No. 2, from a different sample from No. 1, the wire became shorter; and the resistance, which should have fallen ·0745 per cent., actually increased 1·475 per cent., being equivalent to a difference of 1·549 per cent. on the original resistance unaccounted for.

With magnesium No. 1 the actual increase of resistance amounted to 2·16 per cent. on the original resistance, whereas theoretically it should have increased 3·39 per cent., or 1·23 per cent. greater than really took place; or we may say that of the theoretical increase only 54·35 per cent. was visible, showing that the specific conductivity of the wire had risen. Four portions of this wire were tested, and the results were all very near alike.

On examining the results obtained with German silver No. 5 (annealed), which after all is most likely to interest us, owing to its employment in resistance-coils, we find that the total increase was equal to ·454 per cent.; and after deducting ·4 per cent., which is due to increase in length and diminution of section, there still remains unaccounted for ·054 per cent. on the original resistance, or 11·89 per cent. of the whole observed change.

With German silver (hard-drawn) the results are very curious. Here the length actually decreased; and on making the necessary corrections, the resistance should have shown a decrease of ·284 per cent.; but the actual decrease was only equal to ·036 per cent., not low enough by ·248 per cent.; or we may say that of the theoretical decrease only 12·26 per cent. was visible.

On examining the curves from the iron wires Nos. 3 and 4, it will be observed that at the commencement uncoiling produced a very large *increase*, while coiling produced a small *decrease*; but after sixteen operations in one case and twenty-

one in the other, the signs became reversed, and this continued throughout the remaining series of the two wires.

On page 74, vol. vi. of the 'Proceedings of the Physical Society,' I find a paper by Mr. Herbert Tomlinson, in which he says that " the behaviour of nickel is especially worthy of notice, because in it longitudinal traction, when not carried beyond a certain limit, *diminishes* the electrical resistance in spite of the increase of length and diminution of section which ensues."

I have not been able to obtain wires in nickel, but, according to the results obtained, some samples of magnesium appear to have the same property.

At the last moment Prof. Stocker has shown me that in *Die Electricität*, by Wiedemann, it is noted that " the coiling of a copper or iron wire increases, whilst the uncoiling diminishes the specific resistance about 0·003 of the total value of the same."

And, again, in *Die Physik*, vol. iii., by Mousson, that " the coiling of a wire upon a cylinder slightly increases the resistance, in consequence, as is supposed, of tension; uncoiling diminishes it again. Under similar circumstances, the changes amounted to 0·0032 in the case of copper and to 0·0056 in iron, of their total resistances."

It will be observed that both these descriptions are contrary to what I must conclude from my own experiments.

Having made some inquiries from a friend of mine who had charge of the testing department in the cable factory of J. B. Pirelli, F. Casassa et Cie, of Milan, he has supplied me with data which show that the specific conductivity of the copper conductors have fallen in many cases $1\frac{1}{2}$ per cent. during manufacture, and when encased in lead tubes they have often fallen over 2 per cent. In all cases the necessary corrections have been made for increase of length and diminution of section due to strain in passing through the covering machines. Possibly the greater loss in the lead-encased core may be due to a damping-effect from the lead, but the bulk of the increase of resistance must be due to some other cause. These cables were manufactured under very strictly enforced conditions for the Italian State Telegraph-stores; and the tests taken by government officials, ten weeks after they had been sent from the factory, were in all cases within 0·2 per cent. of the final tests in the factory, showing conclusively that the changes were in a great measure permanent.

I have therefore come to a very decided conclusion that the changes in the resistance are not altogether the result of changes in form, and that their cause must be sought for elsewhere.

Many theories have suggested themselves, but none are entirely satisfactory.

One theory was that, in coiling, the decrease of resistance was due to a thickening of the wire on its internal side and a thinning of the external side, thus bringing the centre of area inwards, and so making the actual distance the current would have to travel shorter, which would be equivalent to making the wire shorter; and then on uncoiling, the displacement of the molecules, due to slipping on each other when seeking to regain their original position, would have the effect of increasing their distance apart, and consequently increasing the resistance. But the weak point in this theory is that it will not account for the change of signs which so often takes place, nor will it account for the zinc wires giving increased resistances on coiling.

Another theory, which appears more promising, was that, while being coiled and uncoiled, the wires were subject to strains of a torsional kind, which might be due to their having a certain amount of residual twist in them, owing to the way in which they have been coiled on to the drums on the bench of the wire drawer; and that on being coiled and uncoiled on their bobbins this twist might be increased or decreased, so giving different amounts in the resistance. But from experiments I have made, which seem to me quite conclusive, it appears that although there is a certain amount of twisting and untwisting produced by being wound on to the bobbins, yet this fails to account for the residue of the observed changes.

With reference to the effects on the permanency of value of a set of resistance-coils which are only subjected to one winding, I have not yet sufficient data to lay before you; but, so far as I have gone into this part of the subject, I believe that the immediate alterations on coiling the wires on the bobbins are to a great extent affected by the tension and the speed with which they are wound, the thickness and kind of insulator employed (cotton-covered wires appear to be less affected than silk-covered wires), and also by the diameter of the bobbins on which the wire is wound (the smaller the bobbin the greater the alteration). But further experiments are necessary to put these beyond doubt.

Appended to this paper are a few tables showing the actual readings in the first series of several of the wires tested (these readings include the resistance of the leading wires, ·0274). These, together with the curves (Pl. IX.), may be of some service in assisting to a conclusion as to the probable cause of the changes in the resistance of wires produced by coiling and uncoiling.

	1st Series.		2nd Series.		3rd Series.		4th Series.	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U	·2923	+·0001	·3087	+·0001	·3198	-·0002	·3340	-·0001
C	22	+·0011	88	+·0015	·3196	+·0017	39	+·0017
U	33	-·0001	·3103	+·0001	·3213	-·0002	56	-·0004
C	32	+·0007	04	+·0008	11	+·0017	52	+·0012
U	39	+·0001	12	+·0008	28	-·0004	64	-·0004
C	40	+·0005	20	+·0001	26	+·0011	60	+·0012
U	45	+·0002	28	......	37	-·0002	72	-·0004
C	47	+·0005	28	+·0008	35	+·0007	68	+·0010
U	52	+·0002	36	+·0001	42	......	78	-·0001
C	54	+·0005	37	+·0006	42	+·0007	77	+·0009
U	59	+·0002	43	+·0001	49	......	86	-·0001
C	61	+·0006	44	+·0005	49	+·0008	85	+·0008
U	67	+·0002	49	+·0002	57	......	93	......
C	69	+·0004	51	+·0006	57	+·0007	93	+·0007
U	73	+·0004	57	+·0001	64	......	·3400	......
C	77	+·0004	58	+·0005	64	+·0008	00	+·0005
U	81	+·0003	63	+·0001	72	+·0001	5	+·0002
C	84	+·0004	64	+·0005	73	+·0005	7	+·0007
U	88	+·0003	69	+·0002	78	+·0001	14	+·0002
C	91	+·0003	71	+·0006	79	+·0007	16	+·0004
U	94	+·0004	77	+·0003	86	+·0001	20	+·0002
C	98	+·0003	80	+·0005	87	+·0006	22	+·0004
U	·3001	+·0003	85	+·0002	93	+·0001	26	+·0002
C	4	+·0003	87	+·0005	94	+·0005	28	+·0004
U	7	+·0003	92	+·0002	99	+·0001	32	+·0004
C	10	+·0004	94	+·0004	·3300	+·0005	36	+·0003
U	14	+·0003	98		5	+·0001	39	+·0002
C	17	+·0003			6	+·0006	41	+·0002
U	20	+·0004			12	+·0002	43	+·0003
C	24	+·0004			14	+·0005	46	+·0003
U	28	+·0002			19	+·0001	49	+·0004
C	30	+·0004			20	+·0005	53	+·0003
U	34	+·0004			25	+·0002	56	+·0003
C	38	+·0002			27	+·0006	59	+·0003
U	40	+·0002			33	+·0003	62	+·0003
C	42	+·0003			36	+·0004	65	+·0003
U	45	+·0002			40		68	+·0003
C	47	+·0004					71	+·0004
U	51	+·0005					75	+·0004
C	56	+·0003					79	+·0003
U	59	+·0003					82	+·0003
C	62	+·0004					85	+·0002
U	66	+·0003					87	+·0003
C	69	+·0003					90	+·0003
U	66	+·0004					93	+·0003
C	70	+·0006					96	+·0003
U	76	+·0003					99	+·0003
C	79	+·0004					·3502	+·0003
U	83	+·0004					5	+·0003
C	87	+·0003					8	+·0001
U	90	......					9	
C	90							

2nd Series: Rested here 21 hours ; no change on resuming.

3rd Series: Rested here 22 hours ; no change on resuming.

4th Series: Loss after standing 21 hours = ·0003.

Aluminium Wire.

	No. 1.			
	1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.
U ...	·08004	......	·08042	
C ...	4	+·00018	37	—·00005
U ...	22	—·00007	48	+·00011
C ...	15	+·00011	42	—·00006
U ...	26	—·00008	49	+·00007
C ...	18	+·00010	43	— 00006
U ...	28	—·00006	53	+·00010
C ...	22	+·00010	47	—·00006
U ...	32	—·00007	58	+·00011
C ...	25	+·00009	53	—·00005
U ...	34	—·00007	61	+·00008
C ...	27	+·00010	56	—·00005
U ...	37	—·00011	64	+·00008
C ...	26	+·00009	59	—·00005
U ...	35	—·00005	67	+·00008
C ...	30	+·00008	63	—·00004
U ...	38	—·00005	69	+·00006
C ...	33	+·00008	66	— 00003
U ...	41	—·00006	71	+·00005
C ...	35	+·00009	68	—·00003
U ...	44	—·00005	72	+·00004
C ...	39	+·00007	68	—·00004
U ...	46	—·00004	73	+·00005
C ...	42	+·00006	69	—·00004
U ...	48	—·00004	74	+·00005
C ...	44	+·00005	71	—·00003
U ...	49	—·00003	76	+·00005
C ...	46	+·00006	73	—·00003
U ...	52	—·00004	77	+·00004
C ...	48	+·00007	74	—·00003
U ...	55	—·00003	78	+·00004
C ...	52	+·00008	75	—·00003
U ...	60	—·00004	79	+·00004
C ...	56	+·00005	76	—·00003
U ...	61	—·00003	81	+·00005
C ...	58	+·00003	78	—·00003
U ...	61	—·00002	83	+·00005
C ...	59	+·00003	79	—·00004
U ...	62	-- 00002	82	+·00003
C ...	60	+·00003	79	—·00003
U ...	63	—·00002	82	+·00003
C ...	61	+·00002	80	—·00002
U ...	63	--·00001	82	+·00002
C ...	62	+·00002		
U ...	64	--·00001		
C ...	63	+·00001		
U ...	64	......		
C ...	64	+·00001		
U ...	65	......		
C ...	65	+·00001		
U ...	66			

2nd Series: Rested here 45 hours; and gained by standing ·00019.

1st Series: Rested here 21 hours; less by standing ·00023.

German-silver Wires.

| | No. 4 (hard drawn). | | | | No. 5 (annealed). | | | |
| | 1st Series. | | 2nd Series. | | 1st Series. | | 2nd Series. | |
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U...	1·53483	−·00058	1·53541	−·00096	1·51821	+·00161	1·52150	−·00010
C...	25	+·00037	445	+·00107	982	−·00019	140	+·00010
U...	62	−·00050	552	−·00094	963	+·00018	150	−·00008
C...	12	+·00053	458	+·00087	981	−·00001	142	+·00007
U...	65	−·00052	545	−.00077	980	......	149	−·00011
C...	13	+·00047	468	+·00088	980		138	+·00012
U...	60	−·00055	556	−·00085	980	+·00012	150	−·00014
C..	05	+·00040	471	+·00059	992		136	+·00006
U...	45	−·00043	530	−·00045	992	......	130	−·00008
C...	02	+·00040	485	+·00039	988	−·00004	122	+·00018
U...	42	−·00039	524	−·00044	1·52000	+·00012	140	−·00017
C...	03	+·00039	480	+·00038	1994	−·00006	123	+·00012
U...	42	−·00037	518	−·00036	2004	+·00010	135	−·00015
C...	05	+·00036	482	+·00036	2000	−·00004	120	+·00012
U...	41	−·00041	516	−·00038	2010	+·00010	132	−·00013
C...	00	+·00040	478	+·00023	2003	−·00007	119	+·00010
U...	40	−·00040	501	−·00029	2020	+·00017	129	−·00018
C...	00	+·00036	472	+·00027	2010	−·00010	111	+·00009
U...	36	−·00036	499	−·00033	2025	+·00015	120	−·00012
C...	00	+·00035	66	+·00019	2014	−·00011	108	+·00006
U...	35	−·00039	85	−·00026	2031	+·00017	114	−·00014
C...	1·53396	+·00038	59	+·00021	2021	−·00010	100	+·00015
U...	434	−·00039	80	−·00028	2038	+·00017	085	−·00012
C...	395	+·00039	52	+·00021	2027	−·00011	073	+·00011
U...	434	−·00040	73	−·00036	2040	+·00013	062	−·00006
C...	394	+·00029	37	+·00025			068	+·00003
U...	423	−·00033	62	−·00014	Rested for 16		071	−·00006
C...	390	+·00031	48	+·00014	hours; gained		065	+·00005
U...	421	−·00031	62	−·00028	·00110.		070	......
C...	390	+·00035	34	+·00024			070	+·00001
U...	425	−·00034	58	−·00027			071	−·00001
C...	391	+·00034	31	+·00021			070	+·00002
U..	425		52				072	−·00002
C...							070	+·00003
U...							073	

No. 4 1st Series: Rested for 21 hours; gained ·00116.

No. 4 2nd Series: Rested for 21 hours; gained ·00109.

No. 5 2nd Series: Rested for 26 hours; gained ·00231.

Magnesium Wires.

| | No. 1. Length at commencement = 55·08 inches. | | | | No. 2. Length at commencement = 86 inches. | | | |
| | 1st Series. | | 2nd Series. | | 1st Series. | | 2nd Series. | |
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U…	·29195		·29488		·44079		·44312	
C…	60	−·00135	384	−·00104	3815	−·00264	148	−·00164
U…	210	+·00150	525	+·00141	4148	+·00333	368	+·00220
C…	75	−·00135	410	−·00115	3933	−·00215	205	−·00163
U…	225	+·00150	555	+·00145	4216	+·00283	404	+·00199
C…	98	−·00127	427	−·00128	3991	−·00225	232	−·00172
U…	255	+·00157	567	+·00140	4245	+·00254	381	+·00149
C…	145	−·00110	445	−·00122	4023	−·00222	223	−·00158
U…	265	+·00120	567	+·00122	257	+·00234	385	+·00162
C…	155	−·00110	435	−·00132	062	−·00195	231	−·00154
U…	280	+·00125	565	+·00130	272	+·00210	386	+·00155
C…	180	−·00100	465	−·00100	091	−·00181	235	−·00151
U…	303	+·00123	575	+·00110	300	+·00209	380	+·00145
C…	178	−·00125	473	−·00102	126	−·00174	242	−·00138
U…	277	+·00099	585	+·00112	325	+·00199	381	+·00139
C…	186	−·00091	482	−·00103	168	−·00157	241	−·00140
U…	284	+·00098	594	+·00112	230	+·00062	384	+·00143
C…	185	−·00099	488	−·00106	088	−·00142	246	−·00138
U…	292	+·00107	605	+·00117	248	+·00160	381	+·00135
C…	205	−·00087	496	−·00109	081	−·00167	242	−·00139
U…	295	+·00090	610	+·00114	251	+·00170	380	+·00138
C…	205	−·00090	505	−·00105	089	−·00162	241	−·00139
U…	285	+·00080	617	+·00112	250	+·00161	376	+·00135
C…	225	−·00060	505	−·00112	084	−·00166	244	−·00124
U…	327	+·00102	620	+·00115	245	+·00161	368	+·00129
C…	237	−·00090	525	−·00095	085	−·00160	239	−·00129
U…	345	+·00108	625	+·00100	246	+·00161	370	+·00131
C…	250	−·00095	535	−·00090	100	−·00146	241	−·00129
U…	362	+·00112	622	+·00087	249	+·00149	368	+·00127
C…	265	−·00097	545	−·00077	112	−·00137	240	−·00128
U…	377	+·00102	645	+·00100	251	+·00139	354	+·00114
C…	314	−·00063	547	−·00098			242	−·00112
U…	434	+·00120	647	+·00100			350	+·00108
C…	355	−·00079	566	−·00081			235	−·00115
U…	438	+·00083	660	+·00094			351	+·00116
C…	366	−·00072	573	−·00087			239	−·00112
U…	445	+·00079	667	+·00094			344	+·00105
C…	385	−·00060					238	−·00106
U…	458	+·00073					341	+·00103
C…	390	−·00068					237	−·00104
U…	462	+·00072					342	+·00105
C…	397	−·00065						
U…	468	+·00071						

No. 1, 1st Series: Rested here 21 hours; resistance rose to ·29488; showing gain by standing of ·00020.

No. 1, 2nd Series: Rested here 21 hours; gained ·00021.

No. 2, 1st Series: Rested here 18 hours; gained by standing ·00061.

No. 2, 2nd Series: Rested here 26 hours; gained by standing ·0003.

Iron Wires (soft).

	No. 3				No. 4			
	1st Series		**2nd Series**		**1st Series**		**2nd Series**	
	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.	Resistance.	Difference.
U...	·34735	+·00007	·34995	+·00094	·34720	+·00015	·34970	+·00090
C...	42	+·00032	·35089	−·00067	35	+·00043	·35060	−·00045
U...	74	−·00002	022	+·00071	78	−·00006	15	+·00050
C...	72	+·00040	093	−·00046	72	+·00043	65	−·00037
U...	812	−·00004	047	+·00054	·34815	+·00001	28	+·00046
C...	16	+·00026	101	−·00059	16	+·00021	74	−·00044
U...	42	+·00005	042	+·00045	37	+·00005	30	+·00038
C...	47	+·00015	097	−·00058	42	+·00018	63	−·00033
U...	62	+·00008	039	+·00059	60	+·00008	35	+·00042
C...	70	+·00016	098	−·00050	68	+·00012	77	−·00045
U...	86	+·00016	048	+·00056	80	+·00018	32	+·00038
C...	902	+·00012	104	−·00046	98	+·00022	70	−·00039
U...	14	+·00018	058	+·00049	·34920	+·00010	31	+·00048
C...	32	−·00004	107	−·00050	30	......	79	−·00037
U...	28	+·00028	057	+·00058	30	+·00010	42	+·00046
C...	56	−·00036	115	−·00059	40	−·00010	88	−·00043
U...	20	+·00052	056	+·00061	30	+·00023	45	+·00054
C...	72	−·00020	117	−·00055	53	−·00023	99	−·00030
U...	52	+·00040	062	+·00062	30	+·00038	69	+·00050
C...	92	−·00028	124	−·00066	68	−·00028	·35119	−·00034
U...	64	+·00051	058	+·00060	40	+·00024	085	+·00043
C...	·35015	−·00033	118	−·00042	64	−·00019	128	−·00016
U...	4982	+·00059	076	+·00038	45	+·00020	112	+·00033
C...	5041	−·00039	114	−·00030	65	−·00015	45	−·00021
U...	5002	+·00056	084	+·00034	40	+·00035	24	+·00035
C...	58	−·00039	118	−·00016	75	−·00025	59	−·00015
U...	19	+·00060	102	+·00040	50	+·00048	44	+·00036
C...	79	−·00041	142	−·00021	98	−·00030	80	−·00010
U...	38	+·00058	121	+·00043	68	+·00046	70	+·00029
C...	96	−·00041	164	−·00019	64	−·00026	99	−·00009
U...	55		145	+·00047	·35014	+·00062	90	+·00036
C...			192	−·00016	·34988	−·00028	·35226	−·00007
U...			176		·35050	+·00056	19	+·00049
C...					32	−·00023	68	−·00012
U...					88		56	
C...					65			
U...								

No. 3, 1st Series: Rested here 45 hours; loss by standing = ·060.

No. 3, 2nd Series: Rested here 45 hours; gained by standing = ·00029.

No. 4, 1st Series: Rested here 21 hours; loss by standing ·00095.

No. 4, 2nd Series: Rested here 21 hours; loss by standing = ·00026.

Copper Wire.

| | No. 4. | | | |
| | 1st Series. | | 2nd Series. | |
	Resistance.	Difference.	Resistance.	Difference.
U	·17762		·17882	
C	59	−·00003	·17880	−·00002
U	78	+·00019	·17903	+·00023
C	75	−·00003	·17894	−·00009
U	88	+·00013	·17914	+·00020
C	85	−·00003	04	−·00010
C	97	+·00012	28	+·00024
U	94	−·00003	20	−·00008
C	·17808	+·00014	36	+·00016
U	04	−·00004	30	−·00006
C	25	+·00021	41	+·00011
U	20	−·00005	34	−·00007
C	31	+·00011	48	+·00014
U	27	−·00004	43	−·00005
C	39	+·00012	60	+·00017
U	34	−·00005	52	−·00008
C	43	+·00009	67	+·00015
U	38	−·00005	59	−·00008
C	47	+·00009	73	+·00014
U	43	−·00004	65	−·00008
C	54	+·00011	78	+·00013
U	49	−·00005	71	−·00007
C	60	+·00011	84	+·00013
U	55	−·00005	77	−·00007
C	64	+·00009	89	+·00012
U	59	−·00005	82	−·00007
C	66	+·00007	93	+·00011
U	63	−·00003	87	−·00006
C	71	+·00008	97	+·00010
U	67	−·00004	91	−·00006
C	74	+·00007	98	+·00007
U	70	−·00004	91	−·00007
C	77	+·00007	99	+·00008
U	74	−·00003	96	−·00003
U	·17880	+·00006	·18005	+·00009

Rested here 21 hours; gained by standing ·00002.

Rested here 21 hours; loss by standing ·00039.

Zinc Wires.

	No. 5.		No. 6.	
	Resistance.	Difference.	Resistance.	Difference.
U	·14063	+·00014	·14038	+·00027
C	077	+·00018	065	+·00025
U	095	+·00009	090	−·00003
C	104	+·00024	087	+·00032
U	128	+·00007	119	−·00002
C	135	+·00011	117	+·00021
U	146	+·00003	138	......
C	149	+·00011	138	+·00014
U	160	+·00004	152	−·00003
C	164	+·00009	149	+·00015
U	173	+·00005	164	−·00001
C	178	+·00008	163	+·00015
U	186	+·00004	178	+·00002
C	190	+·00010	180	+·00011
U	200	+·00005	191	+·00002
C	205	+·00007	193	+·00012
U	212	+·00007	205	+·00003
C	219	+·00008	208	+·00010
U	227	+·00012	218	+·00003
C	239	+·00005	221	+·00009
U	244	+·00013	230	+·00005
C	257	+·00004	235	+·00010
U	261	+·00009	245	+·00006
C	270	+·00002	251	+·00019
U	272	+·00006	270	+·00018
C	278	......	288	
U	278	+·00017		
C	295		Wire broke.	

Wire broke.

XLIX. *On the Distance between the Poles of a Magnet, the Coefficients of Temperature and Induction, and on the Determination of Moments of Inertia by means of Bifilar Suspension.* By F. KOHLRAUSCH[*].

WHENEVER a magnet forms the object or means of any measurement, there are especially the following properties to be taken into account. Besides its magnetic moment, the changes in the same with temperature and with the position in the magnetic field play an important part, the distribution of magnetism in the bar, and, as a first approximation, the distance apart of the poles of the magnet is of importance ; and the moment of inertia of the heavy mass has to be taken into account in all the usual methods of observation.

I take the present opportunity of communicating some observations and experiments upon each of these four magnitudes.

The results of the first part of the investigation, undertaken conjointly with Mr. W. Hallock, will appear shortly in detail.

I. *On the Distance Apart of the Poles of Magnets.* *By* W. Hallock *and* F. Kohlrausch[*].

II. *On the Increase and Decrease in Magnetic Moment produced by Small Forces.*

We discuss here a single point, but a fundamental point in the doctrine of induced magnetism. If we expose a steel magnet to the action of feeble forces by which its magnetism is either strengthened or weakened, the question arises whether the increase and decrease in strength are of equal or of different magnitude. Lamont[†] has occupied himself with this inquiry in his extended magnetic researches, and found that the enfeeblement takes place more easily than the reinforcement, and about in the proportion 4 : 3; and this view seems to have been partially accepted by those [‡] who have occupied themselves with the subject. No thorough experimental investigation, however, appears to exist, and yet it is a subject of the greatest importance in the more exact magnetic and electrical measurements. Wild considers the determination of the coefficient of induction as one of the chief difficulties in the measurement of the intensity of terrestrial magnetism, and, to avoid it, even proposes[§] to bring the oscillating magnet into a position at right angles to the meridian by means of a bifilar suspension.

Whilst it must be admitted that there is, in fact, a certain difficulty in the determination of the two different coefficients, yet this is much lessened if we have simply to determine their sum according to the method of induction-currents given by Weber[‖]. If we have established a nearly constant ratio between the coefficients, we of course need only to know their sum.

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[*] A translation of this section was given among the short notices in our last Number, p. 390.

[†] *Erdmagnetismus*, p. 149 (1849).

[‡] Compare (*e. g.*) Wild, *Rep. d. Meteor. d. K. Acad. zu Petersb.* viii. No. 7, p. 61 (1883), where it is mentioned that some observers, amongst them the author, have made no distinction between the coefficient of increase and that of decrease.

[§] Wild, *loc. cit.* pp. 73 & 43.

[‖] *Abh. d. Gött. Ges. d. Wiss.* vi. p. 65 of reprint, 1855. I cannot see that the method suffers from complication, as H. Wild thinks. The accuracy required here at least is to be obtained with very simple apparatus.

It has always appeared to me most probable that this relation must exist, but not in the way assumed by Lamont, but simply as an equality. Lamont's experiments do not seem to be sufficient to justify the view originally taken by him. Later, Lamont appears[*] to return to the former view without expressly saying so. He refers only briefly to some experiments "previously published" by him, but does not mention their result again. On the contrary, he calculates as if both coefficients were of equal magnitude for very small forces, and speaks of this as the generally accepted view.

This latter view is indeed, *à priori*, the most probable, for it corresponds to the law of permanency.

The analogy, employed by Lamont, that a distorted elastic body is more easily caused to return to its natural form than to recede further from it, cannot be considered as of much force. This fact of molecular mechanics is no doubt true for persistent alteration of form. The limit of elasticity of a bent body is, we know, greater outwardly than inwardly; and so, of course, a magnet will in general behave towards forces which are sufficiently great to cause a permanent alteration in its magnetism. But we are not now concerned with that. The change in magnetic moment depending upon change in position relative to the earth is to be compared to elastic changes in form, and for these there is no doubt that the modulus of elasticity is of equal magnitude in both directions.

I have abundantly convinced myself of the correctness of both of these assertions. A magnet which had been exposed some 8000 times to a weakening force of the magnitude of the earth's horizontal magnetism (0·2 centimetre-gramme-unit) showed still the same magnetism as before to within $\frac{1}{2000}$. And, as far as the modulus of elasticity is concerned, I found this the same in both directions in a soft-steel rod which had been just before much bent. I have endeavoured, with the important assistance derived from the observations of M. Kreichgauer, to decide this question in the following manner.

First I employed Weber's method of currents induced in a rotated spiral by the varying magnetism, employing only rotations of 90°; viz. first, from the east and west position of the magnet into the normal position (north pole towards the north), and, secondly, into the reversed position (north pole towards the south). The deflections of the galvanometer-needle in the two cases were found to be perceptibly equal.

A difference of less than 1 per cent. in favour of the coefficient of increase is easily accounted for by a small error in the adjustment of the spiral.

Weber's method becomes more convenient and more exact if, instead of reversing the magnet and spiral with reference to the earth's magnetism, we reverse a magnetic force with reference to the spiral and the magnet in the spiral. For this purpose the induction-spiral was further wound with 280 turns of wire, forming a coil of 5 centim. diameter and a total length of 39 centim., through which a current was passed, producing within the spiral a magnetic field of about 0·2 C.G.S. unit, and thus of about the same strength as the earth's horizontal magnetism. This current was made or interrupted so as to increase or to diminish the magnetism of the bar. Momentary currents were thus induced in the inner spiral, which were measured by the method of multiplication. Moreover, the part of the induced current resulting from the magnetizing current itself could be compensated by means of a second duplicate spiral, which is an advantage of this electromagnetic method. A similar arrangement has already been described by Töpler and Von Ettingshausen[*]. Local disturbances are eliminated by reversal of the current and magnet.

In order to infer the induced magnetism from the deflections of the galvanometer, a small magnet of known moment was employed, by the use of which experiments according to the method of multiplication could be made by introducing the magnet into the spiral and withdrawing it.

The steel bars were examined in various conditions of hardness and intensity of magnetization, as detailed in the first column of the following Table. The mass m of the bars is given in grammes, the magnetic moment in centimetre-gramme units, and under s the specific magnetism $\dfrac{M}{m}$ or the magnetic moment per gramme of steel.

Lastly, under $+\Delta s$ and $-\Delta s$ are given the specific induction constants; so that the numbers denote the change in specific magnetism; in other words, the increase or decrease in the magnetic moment of the unit of mass (1 gr.) which is produced by the unit of magnetizing or demagnetizing force ($\mathrm{gr.}^{\frac{1}{2}}$ cm.$^{-\frac{1}{2}}$ sec.$^{-1}$).

By way of explanation, it may be observed that the number Δs represents nearly the change in specific magnetism produced in our latitudes by reversing the bar in the direction of the dip-needle. About the fifth part is the "magnetism of position" produced in 1 gr. in our latitude by the earth's horizontal magnetism[†].

[*] Pogg. *Ann.* clx. p. 1 (1877).
[†] Multiplied by 7·6 (the density of steel) the numbers s or Δs give the specific magnetism or induction-constant (as the case may be) referred to unit volumes, which latter, as Herwig has remarked, represent absolute numbers, and are thus independent of the units employed.

	$m.$	M.	$s = \dfrac{M}{m}$	$+\Delta s$	$-\Delta s.$
	g.	$\dfrac{cm^{\frac{5}{2}} g^{\frac{1}{2}}}{sec}$	$\dfrac{cm^{\frac{5}{2}}}{g^{\frac{1}{2}} sec}$	$\dfrac{cm^3}{g}$	
Cylinder, 16 cm. long, 1·5 cm. thick, hard	} 216				
Ditto, magnetized a year ago......	...	4200	20	+0·202	−0·201
Ditto, newly magnetized............	...	6200	29	+0·218	−0·214
Ditto, often magnetized and heated for a long time	} ...	5000	23	+0·216	−0·215
Hollow cylinder 16 cm. long, internal and external diameter 1·2 and 1·6 cm. respectively.........	} 109				
Ditto, magnetized and heated a year ago	} ...	3500	32	+0·261	−0·265
Ditto, newly magnetized............	...	4200	38	+0·261	−0·264
Parallelopiped 18×1·5×0·5 cm.	114				
Ditto, soft, unmagnetized	...	0	0	+0·459	
Ditto, soft, magnetized	..	940	8·3	+0·447	−0·449
Ditto, hard, unmagnetized	..	0	0	+0·335	
Ditto, hard, magnetized	...	3600	32	+0·308	−0·305
Parallelopiped 18×1·7×0·6 cm.	144				
Ditto, soft, unmagnetized	...	0	0	+0·490	
Ditto, soft, magnetized	...	1230	8·6	+0·467	−0·465
Ditto, hard, unmagnetized	...	0	0	+0·341	
Ditto, hard, magnetized	...	3900	27	+0·303	−0·304

There is no decided difference in any one of these numbers between the coefficient $+\Delta s$ of increase of strength and the coefficient of decrease in strength $-\Delta s$.

The small differences of irregular sign are due to errors of observation, and are caused, for the most part, by variations in the strength of the inducing current. The mean values show exact equality.

It is thus proved that there is no inequality in the coefficients of increase and decrease of any such proportion as 3 : 4 or anything like it; but that for practical purposes we need only admit one coefficient of change of magnetism produced by external forces, whether they tend to increase or to decrease it. This is, of course, true only within certain limits; how far these limits extend must be left for further investigation. I will only remark here that, with forces which amount to about half of the earth's horizontal magnetism, more or less, we arrive practically at the same numbers.

It appears from these results that this subject has been invested with unnecessary difficulty. One other point, it is true, remains undecided, viz. the question whether, and under what circumstances, a change of the induced magnetic moment with time can be disregarded. Without doubt such an influence exists, but for magnets of hard steel it may no doubt be neglected in practice.

III. *On the Determination of the Temperature Coefficient of a Magnet.*

The following general and sensitive method may be added to the known methods of W. Weber and Lamont. The bar to be examined is brought near to a reflecting magnetic needle in the horizontal plane of the needle so that its centre point lies in the meridian of the needle, and so that it, acting together with the earth's magnetism, brings the needle into an east-and-west position. Let the bar in this position make an angle ϕ with the meridian. If now the magnetism M of the bar change by an amount ΔM, the needle will alter its position by the small angle $\Delta\epsilon$. Then, apart from corrections (compare below), it is easily seen that we have

$$\frac{\Delta M}{M} = \tfrac{1}{2}\tan\phi \,.\, \Delta\epsilon.$$

We observe that this method may be made very sensitive by choosing the distance of the magnet from the needle so that the angle ϕ shall be small.

For the practical employment of this method it is very convenient to have the magnetic bar on the rotating arm of a graduated circle. As a magnetic needle I have employed a steel disk with reflecting surfaces. The method of procedure is then as follows:—

In order to measure the angle ϕ, the magnetic bar is rotated from its original position until the image of the scale is seen in the second reflecting surface. This rotation amounts then to 2ϕ. The rotating arm in the two positions differing by 2ϕ, is struck, and the magnet rotated in each observation between the strokes, *i. e.* when cold and when hot. The influence of small unintentional rotations of the magnetic axis of the bar, such as might be produced by the heating itself, is thus avoided.

Let A be the distance of the scale from the mirror at the one temperature t. Let the positions ϵ_1 and ϵ_2 of the needle be observed upon rotation of the bar through the angle 2ϕ, and at the other temperature t' the positions ϵ'_1 and ϵ'_2. If we denote $\epsilon_1 - \epsilon_2$ by n and $\epsilon'_1 - \epsilon'_2$ by n', then the relative loss of magnetism,

$$\frac{\Delta M}{M} = \frac{\tan\phi}{8A}(n-n');$$

and the temperature-coefficient therefore,

$$\theta = \frac{\tan\phi\,(n-n')}{8A(t-t')}.$$

Corrections for the Length of the Rod.—It would not be practicable to make the distance of the magnet from the needle so great that the length of the bar might be neglected ; since for a considerable distance there would exist no angle ϕ which would bring the needle into a transverse position. We may take account of the length of the rod by multiplying the above result by

$$1 + \tfrac{1}{8} \frac{\lambda^2}{a^2} (3 + 5 \cos^2 \phi).$$

In this a is the distance of the middle point of the magnet from the needle, λ the distance apart of the poles of the magnet—that is, in the case of bar-magnets, five sixths of the length of the bar.

IV. *On the Bifilar Determination of Moments of Inertia.*

Gauss's well-known method of determining the moment of inertia of a body from its oscillations, when loaded and in the unloaded condition, eliminates the unknown directive force of the oscillations. The employment of a known directive force (*e. g.* of a bifilar* directive force) permits the employment of a simpler method.

I was induced to investigate this method of determination by obtaining, by means of suspended weights, inconsistent measurements of the moment of inertia of a magnetic bar, and, in spite of the greatest care, a result too great, as could be concluded from geometrical measurement of the carefully worked bar.

The method was carried out by means of the bifilar-suspension arrangement recently described by me†. We determine first the moment of inertia of the bifilarly-suspended carrier

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* Kohlrausch, Wied. *Ann.* xvii. p. 744 (1882).

† By adopting the extremely convenient method of M. Wild, in which the oblique surfaces over which the wires run are replaced by surfaces at right angles to which the wires are clamped (*Rep. f. Meteor. d. K. Acad. d. Wiss. St. Petersb.* vii. No. 7, 1883).

I may be allowed to remark here that I am quite unable to regard my method of the "bifilar" measurement of the earth's magnetic intensity as a combination of Gauss's method with that of Wild, as M. Wild appears to do (*loc. cit.* p. 2). I believe that I may claim for my method that it is an altogether independent one. For the "bifilar galvanic method," out of which the "bifilar magnetic" has been evolved, is found described, long before the first of the publications of M. Wild on this subject, and with account taken of the torsion of the threads, in the third edition of the *Leitfaden der praktischen Physik*, 1877, p. 184. The first bifilar-magnetic method described by Wild in the year 1881 is, further, altogether different from mine both in arrangement and in object. Wild's second method is more nearly like mine, but it was unknown to me, since it was published later than mine.

by means of the well-known relation between the oscillation-period t, the bifilar directive force, and the moment of inertia $K = \dfrac{D t^2}{\pi^2}$; then the body to be investigated is laid in the carrier, and the moment of inertia of both is determined in the same way.

I must refer to my former paper[*] for the method of determining the directive force D from the distance apart, the length, weight, and elasticity of the suspension-threads, and the weight of the body, as well as for details of instrumental adjustment and observation.

If the body is magnetic, we have to eliminate from the bifilar direction-force that arising from the earth's magnetism with the relatively small magnitude of the latter. This is easily done by arranging that during the oscillations the magnet shall lie east and west. Or we may bring the suspension with the magnet into the meridian, and observe the oscillation-period t_1 in the normal position and t_2 in the reversed position of the magnet. Then the oscillation-period of the unmagnetized body would be

$$\sqrt{2}\,\frac{t_1 t_2}{\sqrt{t_1^2 + t_2^2}}.$$

Lastly, the measurement of moment of inertia may be made before the body is magnetized.

It is a matter of course that the requisite care should be bestowed upon the adjustment of the centre of gravity[†].

The oscillations are performed generally very rapidly, much more so than one is accustomed to with swinging magnets. The observations, however, may be made with the same accuracy. We simply note the times of reversal on each side, in doing which we may, if necessary, omit one or more.

The accuracy which may be attained is not inferior to that which may be obtained with slower vibrations. I found the results of separate observations, when the oscillation-period amounted to about 1 second, to agree to within a few ten-thousandths of a second.

The moments of inertia of the magnetic bar mentioned before (16 centim. long, 216 gr. weight) agreed very well with each other, as well as with that calculated from its dimensions.

The following may be mentioned as advantages of the bifilar mode of determination:—

[*] F. Kohlrausch, Wied. *Ann.* xvii. pp. 744 & 745 (1882).
[†] F. Kohlrausch, *loc. cit.* p. 754.

(1) The avoiding of the principal errors of weights simply hung on*, or the uncertainty resulting from the possible heterogeneous nature of solid bodies used as loads, as, for example, Lamont's ring.

(2) The avoiding of variations of a magnetic directive force by the temperature and terrestrial magnetic variations.

(3) The greater simplicity of repeating a determination by means of a single oscillation-period when the moment of inertia of suspension has been determined once for all.

(4) The avoiding of the influence of layers of air vibrating with the body, or of any possible magnetic induction upon the weights used as load.

L. *On* Hamilton's *Quadratic Equation and the general Unilateral Equation in Matrices.* *By* J. J. SYLVESTER, *F.R.S., Savilian Professor of Geometry in the University of Oxford*†.

IN the Philosophical Magazine of May last I gave a purely algebraical method of solving Hamilton's equation in Quaternions, but did not carry out the calculations to the full extent that I have since found is desirable. The completed solution presents some such very beautiful features, that I think no apology will be required for occupying a short space of the Magazine with a succinct account of it.

Hamilton was led to this equation as a means of calculating a continued fraction in quaternions, and there is every reason for believing that the Gaussian theory of Quadratic Forms in the theory of numbers may be extended to quaternions or binary matrices, in which case the properties of the equation with which I am about to deal will form an essential part of such extended theory‡. Let us take a form slightly more general than that before considered, viz. the form

$$px^2 + qx + r = 0,$$

with the understanding that the determinant of p (if we are dealing with matrices), or its tensor if with quaternions, differs

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* Compare Dorn, Wied. *Ann.* xvii. p. 788 (1882), and O. Beling, 'On the Theory of Bifilar Suspension ' (Breslau, 1881).

† Communicated by the Author.

‡ I have found, and stated, I believe, in the form of a question in the 'Educational Times' some years ago, that any fraction whose terms are real integer quaternions may be expressed as a finite continued fraction, the greatest-common-measure process being applicable to its two terms, provided *both* their Moduli are not odd multiples of an odd power of 2, which can always be guarded against by a previous preparation of the fraction.

from zero. Let us construct the ternary quadratic

$$au^2 + 2buv + 2cuw + dv^2 + 2evw + fw^2,$$

defined as the determinant of $up + vq + wr$, on the one supposition, or by means of the equations

$$a = \mathrm{T}p^2, \quad d = \mathrm{T}q^2, \quad f = \mathrm{T}r^2; \quad b = \mathrm{S}p\mathrm{S}q - \mathrm{S}\mathrm{V}p\mathrm{V}q,$$
$$c = \mathrm{S}p\mathrm{S}r - \mathrm{S}\mathrm{V}p\mathrm{V}r, \quad e = \mathrm{S}q\mathrm{S}r - \mathrm{S}\mathrm{V}q\mathrm{V}r,$$

on the other supposition.

On referring to the article of May, it will be seen that the solution of the equation may be made to depend on the roots of a cubic equation in the quantity therein called λ. When fully worked out, this equation will be found to take the remarkable form $e^{\lambda\Omega} \cdot \mathrm{I} = 0$, where I is the invariant of the ternary quadratic above written, and $\Omega = 2a\delta_c - a\delta_d$. It may also be shown that

$$x = -\frac{(p+b-u)(q-c-u)}{2\lambda},$$

where u is a two-valued function of λ, and v a linear function of u.

I shall suppose that I, the final term in the equation in λ, differs from zero: the solution of the given equation in x will then be what may be termed *regular*, and will consist of three pairs of actual and determinate roots. When I $= 0$, the solution ceases to be regular; some of the roots may disappear from the sphere of actuality, or may remain actual but become indeterminate, or these two states of things may coexist. The first coefficient of the equation in λ is a, the determinant of p (or its squared tensor), which also must not be zero, as in that case one root at least of λ would be infinite. Let us suppose, then, that neither a nor I vanishes. The very interesting question presents itself as to what kind of equalities can arise among the *three* pairs of roots, and what are the conditions of such arising.

This equation admits of an extremely interesting and succinct answer as follows:—Let m represent $\dfrac{c+2d}{3}$; the equalities between the roots of the given equation in x will be completely governed, and are definable by the equalities existing between those of the biquadratic binary form

$$(a, b, m, e, f)(\mathrm{X}, \mathrm{Y})^4 \, *.$$

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* If the equation is regarded as one in quaternions, the determining biquadratic is the modulus of $x^2 + xp + q$; from which it follows immediately that, if p, q are *real* quaternions, all the four roots, say α, β, γ, δ,

If the biquadratic has two equal roots, the given quadratic will have two pairs of equal roots.

If the biquadratic has two pairs of equal roots, the given quadratic will have four equal roots.

If the biquadratic has three equal roots, the quadratic will have three pairs of equal roots.

If the biquadratic has all its roots equal, the quadratic will have all its roots equal.

In the first case two of the three pairs of roots of the given quadratic coincide, or merge into a single pair.

In the second case, not only two pairs merge into one pair, but the two roots of that pair coincide with one another.

In the third case the three pairs merge into a single pair.

In the fourth case the two members of that single pair coincide with one another.

So long as the equation in x remains regular, no kind of equalities can exist between the roots other than those above specified.

For instance, let us consider the possibility of two values of x, and no more, becoming equal. First, let us inquire what is the condition to be satisfied in order that the scalar parts of two roots which belong to the same pair shall become equal. It may be shown that the sufficient and necessary condition that this may take place is that the irreducible subinvariant of degree 3 and weight 6 (*i. e.* the first coefficient of the irreducible skew-covariant of the associated biquadratic form $[a, b, m, e, f]$) shall vanish.

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are imaginary. It may be shown that the roots of Hamilton's determining cubic are

$$d - \frac{(\alpha+\beta)(\gamma+\delta)}{4}, \quad d - \frac{(\alpha+\gamma)(\beta+\delta)}{4}, \quad d - \frac{(\alpha+\delta)(\beta+\gamma)}{4},$$

and these therefore are (as shown also by Hamilton) all of them real. The biquadratic serves to determine the points in which the variable conic associated to the equation $px^2 + qx + r$ (*i. e.* the determinant to $xp + yq + zr$) is intersected by the absolute conic $xz - y^2$. Each root of the given equation corresponds to a side of the complete quadrilateral formed by the four points of intersection of these two conics; and thus we see that there are five cases to consider when the variable conic is a conic proper, according as it intersects or touches the fixed conic (which can happen in four different ways); and seven other cases where the conic degenerates into two intersecting or two coincident lines (in which cases the solution becomes irregular); viz. the intersecting lines may cut or touch in one or two points the fixed one, and may cut or touch the conic at their point of intersection, which gives five cases; and the coincident lines may cut or touch the fixed conic, which gives two more. Hence there are in all twelve principal cases to consider in Hamilton's form of the Quadratic Equation in Quaternions: or rather thirteen, for the case of the variable and fixed conic coinciding must not be lost sight of.

If, now, the *vectors* as well as the *scalars* of the two roots are to be equal, it may be shown that the *second* as well as the first coefficient of the skew-covariant must vanish. But this cannot happen without the discriminant vanishing*; for it may easily be seen that the discriminant of a binary biquadratic with its sign changed is equal to sixteen times the product of the first and last coefficient, less the product of the second and penultimate coefficients of its irreducible skew-covariant. Hence when two roots belonging to the same pair of the given quadratic coincide, two values of λ become equal, and therefore all four roots belonging to two pairs merge into one.

Again, it is not possible for two roots belonging to two pairs corresponding to two different values of λ to coincide; for in such case the expression given for x shows that pq, p, q, 1 would be connected by a linear equation. But when this happens (as has been shown by me elsewhere), the invariant of the associated ternary quartic vanishes and the equation ceases to be regular. Thus, then, it appears that it is impossible for a single relation of equality (*and no more*) to exist between the roots of the given equation when its form is regular. So, again, it may be shown that it is impossible for four, and no more, relations of equality to exist between the roots.

It need hardly be added, that the equation $px^2 + qx + r = 0$ ceases to be regular when q or r vanishes.

The reader may satisfy himself as to the truth of what has been alleged as to the relation of the discriminant of a binary biquadratic to the coefficients of its skew-covariant by simple verification of the identity

$$16(a^2d - 3abc + 2b^3)(e^2b - 3edc + 2d^3)$$
$$- (a^2e + 2abd - 9c^2a + 6b^2c)(e^2a + 2edb - 9ec^2 + 6d^2c)$$
$$= 27(ace + 2bcd - c^3 - b^2e - ad^2)^2 - (ae - 4bd + 3c^2)^3.$$

The biquadratic equation in X, Y is what the determinant of $\lambda p + \mu q + \nu r$ becomes when X^2, XY, Y^2 are substituted therein for λ, μ, ν; so that we may say that $(a, b, m, e, f)(x, 1)^4$ is the determinant of $px^2 + qr + r$, when x is regarded as an ordinary quantity. Let ϕx be any quadratic factor of this biquadratic function in x: I have found that $\phi x = 0$ will be the *identical* equation to one of the roots of the given equation $fx = 0$, where $fx = px^2 + qx + r$.

Between the two equations $fx = 0$, $\phi x = 0$, x^2 may be elimi-

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* The first two coefficients of the skew-covariant vanishing implies the existence of two pairs of equal roots and *vice versâ*. This is on the supposition made that a, the first coefficient of the given quartic, is not zero.

nated and x found in terms of known quantities: ϕx will have six different values, which will give the six roots of $fx = 0$. It is far from improbable that a similar solution applies to a unilateral equation $fx = 0$ of any degree n in matrices of any order ω.

Call $\mathbf{F}x$ the determinant of fx when x is regarded as an ordinary quantity; then, if ϕx is an algebraical factor of the degree ω in x contained in $\mathbf{F}x$, it would seem to be in all probability true that $\phi x = 0$ is the identical equation to one of the roots of $fx = 0$; and, *vice versâ*, that the function identically zero of any such root is a factor of $\mathbf{F}x$. By combining the equations $fx = 0$, $\phi x = 0$, all the powers of x except the first may be eliminated, and thus every root of x determined. The solution of the given equation will depend upon the solution of an ordinary equation of the degree $n\omega$, and the number of roots will be the number of ways of combining $n\omega$ things ω and ω together. Thus, for a cubic equation in quaternions the number of roots would be $\dfrac{6 \cdot 5}{2}$, or 15. In the May Number of this Magazine it was supposed to be shown to be 21; but it is quite conceivable that this determination may be erroneous, especially as it was deduced from general considerations of the degrees of a certain system of equations without attention being paid to their particular form, which might very well be such as occasion a fall in the *order* of the system. I am strongly inclined, with the new light I have gained on the subject, to believe that such must be the case, and that the true number of roots for a unilateral equation in quaternions of the degree n is $2n^2 - n$ [*]; in which case the theorem above stated, and which may be viewed as a marvellous generalization of the already marvellous Hamilton-Cayley Theorem of the identical equation, will be undoubtedly true for all values of n and ω. But I can only assert positively at present that it is true for the case of $n = 1$ whatever ω may be, and for the case of $n = 2$, $\omega = 2$ [†].

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[*] From the number 21 above referred to, now known to be erroneous, the general value was inferred to be $n^3 - n^2 + n$, whereas it is demonstrably $2n^2 - n$ only for the *general* unilateral equation of degree n in quaternions, as I proved it to be for the *Jerrardian* form of that equation.

[†] I have since obtained an easy proof of the truth of the conjectural theorem for all values of n and ω; see the *Comptes Rendus* of the Institute of France for October 20th last.

LI. *Proof of* Professor Sylvester's *"Third Law of Motion."* *By* Arthur Buchheim, *M.A.*[*]

THE "third law of motion" in the theory of matrices is that "the nullity of the product of two matrices is not less than the greater of their nullities, but not greater than the sum of the two nullities." Prof. Sylvester has given an outline of a proof of this theorem (which he regards as "perhaps the most important in the whole theory of multiple quantity") in his lecture "On the three Laws of Motion in the World of Universal Algebra;"[†] but I have his authority for stating that he considers this proof as wanting in simplicity, so far as the superior limit is concerned. The instantaneous proof here given is merely an extension of the proof given by Clifford for ternary matrices.

A linear space of $(\alpha-1)$ dimensions will be called an α-point: the coordinates of any point of an α-point are linear functions of the coordinates of α points determining it. A matrix A of order n^i is considered as operating on the coordinates of the points of an n-point. Calling the coordinates $(x_1 \ldots x_n)$, there are in general n points satisfying the equations $A(x_1 \ldots x_n) = \lambda(x_1 \ldots x_n)$, where λ is a scalar: λ is one of the latent roots of A, and the point $(x_1 \ldots x_n)$ is called the latent point appertaining to λ. It follows from known theorems on the solution of linear equations, that if A is of nullity α, the equation $A(x_1 \ldots x_n) = 0$ is satisfied by all the points of a certain α-point, and conversely. I call this α-point the *null space* of A, and I denote it by R: any point of R may be said to be *destroyed* by A. There is also an $(n-\alpha)$-point S, which I call the space *preserved* by A: all the points of the n-point which are not destroyed are transformed into points of S: S is, in fact, the $(n-\alpha)$-point determined by the latent points appertaining to the latent roots that do not vanish.

Now let B be a matrix of nullity β; let R' be its null space, and S' the space preserved by it: then I prove that, if R, S' intersect in a δ-point (T), the nullity of AB is $\beta + \delta$.

To find the nullity we have only to find the most general space (the space of most dimensions) that B transforms into T; for this is obviously the most general space destroyed by AB. Now let U be the δ-point in S which B transforms into T; then it is easy to see that the most general space which B transforms into T will be the $(\delta + \beta)$-point joining (U, R'). From this it follows that the *most general* space destroyed by AB is a $(\delta + \beta)$-point—that is, that the nullity

of AB is $\beta + \delta$. If R, S′ do not intersect at all, the most general space destroyed by AB is obviously R′; and the nullity of AB is therefore β.

We have now to distinguish cases : I assume $\alpha + \beta \, \overline{\overline{\lessgtr}} \, n$, which gives $\alpha \, \overline{\overline{\lessgtr}} \, n - \beta$. An α-point and an $(n-\beta)$-point in the same n-point will in general intersect in an $(\alpha-\beta)$-point: therefore if $\alpha \, \overline{\lessgtr} \, \beta$, R, S′ will not intersect at all, but may cut in anything up to an α-point. If $\alpha > \beta$ they may intersect in anything from an $(\alpha-\beta)$-point to an α-point. We therefore have the following theorem :—Let A, B be two matrices of nullities α, β respectively: then, if $\alpha \, \overline{\overline{\lessgtr}} \, \beta$, the nullity of AB is in general β, but may be anything from α to $\alpha + \beta$ inclusive; if $\alpha > \beta$, the nullity of AB is in general α, but may be anything from α up to $\alpha + \beta$ inclusive.

The Grammar School, Manchester,
October 6, 1884.

LII. *Notices respecting New Books.*

Geology of Wisconsin. Survey of 1873–79. Vol. IV. Accompanied by an Atlas of Maps. Large 8vo, pages xxiv & 779. With numerous maps, plans, plates, and woodcuts. [Madison.] 1882.

THIS handsome, well-stored, and richly illustrated volume of the Wisconsin Geological Survey Reports is a worthy successor to the Volumes II. and III., already noticed in the Philosophical Magazine for April 1880 and September 1882. It is divided into nine Parts, being reports and memoirs by members of the Survey and other competent workers.

In Part I. (pages 1–98) Moses Strong gives the " Geology of the Mississippi region north of the Wisconsin River :" noting, first (pp. 3–6), the field-work in general, during 1873–6; then (pp. 7–36), the Physical Geography and Surface-Geology of the district, according to the Townships in their order; thirdly (pp. 38–98), the local Geological Formations are described. These stand thus :—

Periods.		Epochs.	Epochs in Western Wisconsin.
	Quaternary ...	Recent.........	Recent.
		Champlain ...	Champlain.
		Glacial	Glacial.
Lower Silurian.	Trenton	Cincinnati ...	Wanting.
		Utica	Wanting.
		Trenton	Galena, and Blue and Buff Limestones.
	Canadian	Chazy	St.-Peter's Sandstone.
		Quebec	Wanting.
		Calciferous...	Lower Magnesian Limestone.
	Primordial or Cambrian...	Potsdam......	Potsdam Sandstone.
		Acadian	Wanting.
	Archæan	Archæan......	Not exposed.

The lithological and other characteristics of each formation are duly described, together with the economic products, fossils, and places where they are found. The artesian wells and mineral springs of Sparta, Oil-City, La Crosse, Prairie-du-Chien, Jordan, and the water-supply from the Potsdam Formation,—also the Drift and Boulders of the great river-valleys, and the Caves and " Sinks " are especially described.

Part II. (pp. 99–159), by Mr. L. C. Wooster, is a description of the "Lower St.-Croix District." Under "General Geology" we find an account of:—(1) the exposure of the Archæan rocks, as a granite at Chippewa Falls : (2) the Potsdam Group, as the Eau-Claire Grit, the Eau-Claire Trilobite-beds, the Hudson Trilobite-beds with the variable Lower and Upper Calcareous Bands ; (3) the Lower Magnesian Limestone ; (4) St.-Peter's Sandstone ; (5) the Trenton Limestone. The Quaternary formations and their history form an interesting chapter here. The " Hydrology " and the " Vegetation " of the district succeed. The latter comprises the following classes :—1. Prairie and terrace group. 2. Oak and Poplar group. 3. Hardwood and Conifer group. 4. Pine group. 5. Grass and Sedge group. 6. Tamarac group. The mutual relations of vegetation, soil, rainfall, and subjacent rock are here treated of ; and the nature of the soils, peat, brick-earth, &c., is the subject of Chapter VI.

Part III. (pp. 161–349) is a comprehensive account, by Prof. R. P. Whitfield, of the most prominent and characteristic Fossils discovered at different times in Wisconsin, with a general view of the Palæontology of the State, and detailed descriptions of some new fossils. The illustrations consist of 27 good plates. These are species from the Potsdam Sandstone, the Lower Magnesian Limestone, the Trenton- and more particularly the Galena-limestone, and Hudson-River and Niagara Groups, and the Guelph Limestone, and from the Lower Helderberg and the Hamilton (Devonian) Groups. An important Appendix (pp. 350–363) gives a general list of the Fossils hitherto recognized as occurring in the State of Wisconsin, with their respective Geological formations.

Prof. T. C. Chamberlin, the Chief Geologist of the State Survey, has supplied Part IV., fully descriptive of the " Ore-deposits of South-western Wisconsin " (pages 367–568), noticing previous accounts and theories by Owen, Whitney, Murrish, and others, and entering carefully into the subject, with remarks on the nature of the minerals concerned and the grouping of the ores, thus :— I. Minerals in the form first deposited, as galenite, sphalerite, pyrite, marcasite, chalcopyrite, manganese, sulphide, calcite, dolomite, quartz, and barite. II. Secondary Minerals—sulphur, melanterite or copperas, alum, hematite, lemonite or yellow ochre, siderite, cerussite (lead-carbonate), anglesite (lead-sulphate), smithsonite, hydrozincite, goslarite, malachite, azurite, gypsum, and pyrolusite. The areas and special distribution of the ores, the strata containing them, and the local conditions of those strata, the aspect and characters of the lodes, the relations of the ores

to the strata and to each other, and their changes, are all carefully treated, and well illustrated with more than 60 cuts, besides maps. The theoretical deductions as to the origin of the ores occupy Chapter II. of this Part. The hypotheses of sublimation and of thermal waters being objected to, the theory of oceanic deposition and formation from the containing strata is treated in detail, and illustrated by a highly suggestive map of the probable " Silurian Interior Sea," with its currents and islands. Practical considerations follow, as to prospecting and mining ; and an Appendix gives some particulars as to the statistics of Copper-production at Mineral Point.

Part V. (pages 573–581) consists of an account of the " Quartzites of Barron and Chippewa Counties," compiled from the notes of Messrs. Strong, Sweet, Brotherton, and Chamberlin.

Part VI. (pages 583–615), by F. H. King, on the Geology of the Upper Flambeau Valley, comprises the unfinished work of the late Mr. Moses Strong ; and, though full of excellent detail, is rather a report of progress than a complete monograph, the river-courses alone having been examined in the limited period of Survey. The Archæan (Laurentian) rocks are here exposed as granites, gneisses, mica-schists, hornblende-schists, and other old rocks ; some granatiferous *, others with chlorite, kyanite, staurotide, tourmaline, quartz, magnetite, &c. The hydrology, topography, glacial features (scorings, kettles, drift-ridges, till, boulders, &c.), soil, and vegetation of the district are duly considered ; and a microscopical examination of the Archæan rocks, by R. D. Irving, is added (pp. 616–621).

Pages 623–714 contain Part VII., treating of the " Crystalline Rocks of the Wisconsin Valley," by R. D. Irving and C. R. Vanhise. In vol. ii. these rocks were briefly described as far as then observed ; further field-work by members of the Survey has extended the Geological Map and increased the collections. The results are here shown in one general Geological Map and eight sketch-maps of successive portions of the valley, with accompanying notes. A tabulation of the results of Mr. Vanhise's microscopic study of the crystalline rocks of each of these districts supplies the number of the specimen †, a reference to the pages in vol. ii., the name of the rock and of the place, the number of the Land-section, the Town, and the Range on the Sketch-map, the macroscopic description of the rock, and its constituents as determined by the microscope. Granites (hornblendic, augitic, &c.),

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* The use of the base word " garnetiferous " in the Report is as bad as the other bastard word " diamondiferous," in circulation among our South-African colonists.

† The stated numbers of the specimens are the original collection numbers ; and corresponding specimens " will be found in the Cabinets of the State University, and of the Wisconsin Academy of Sciences, and, less completely, in those of the State Normal Schools, of Beltoit, Racine, Ripon, and Milton Colleges, and of Lawrence University."

gneisses, granitells, augite-schists, hornblende-schists, chlorite-schists, mica-schists, porphyries, olivine-diabases, peridotite, diorites, uralitic gabbros, altered porphyritic diabase, norites, vein-quartz, magnetic siliceous schist, argillaceous quartz-schists, and quartzites, are the chief kinds of rock here treated of. Mr. Irving's "summary of results" (pp. 712–714), as to the local extent and the relationships of these great schistose masses, of Huronian and probably Laurentian ages, with their associated eruptive rocks, is concise and useful. He says in conclusion :—"Mr. Vanhise's study shows now that augite, so far from being a stranger to such rocks as gneiss and granite, is nearly as common a constituent, so far at least as this region is concerned, as hornblende or mica, and that all the hornblende of the rocks of this region is but altered augite. My own examinations of many hundred sections of the eruptive rocks of the Copper-bearing Series of Lake Superior have convinced me that in those rocks also there is no hornblende that is not secondary; and, while I am not at all prepared to say that there is no such thing as original hornblende in the older crystalline rocks, I am sure that there is far less of it than has heretofore been supposed. Many diorites are, thus, but uralitic or altered diabases and gabbros; while many syenites, hornblende-granites, hornblende-gneisses, and hornblende-schists are also but altered augitic rocks. The existence of this wide-spread alteration, and of another equally important one, which I have elsewhere shown to obtain widely in the rocks of the Lake-Superior region, namely, the substitution of secondary quartz for primary felspars, makes it very evident to me that any one attempting to solve the problem of the origin of the crystalline schists must give much attention to the matter of internal alterations and replacements."

Part VIII. (pp. 715–723), based on the observations of Mr. A. C. Clarke, and edited by the Chief Geologist, Prof. T. C. Chamberlin, is a succinct notice of the "Superficial Geology of the Upper Wisconsin Valley;" treating of its glaciation, the valley-flood-deposits, earlier glacial deposits, morainic accumulations, boulder-clay or till of the Second Glacial Epoch, peculiarities of drainage, soils, and native vegetation.

Part IX. (pp. 725–754) is a concise account of the "Geological Survey," being a "sketch of the geodetic work done in the State since 1874, under the auspices of the United-States Coast and Geodetic Survey, together with a short outline of the principles and methods pursued in the triangulation, accompanied by two maps, one showing the triangulation executed and proposed, and the other the difference between the positions of the trigonometrical stations as given by ordinary surveys and the same in their true position on the Spheroid." By John E. Davies, Professor of Physics in the University of Wisconsin, and Chief of the Geodetic Survey in Wisconsin. With an Appendix by C. A. Schott, Chief of the Computing Division of the U. S. Geod. Survey, on "the measurement and resulting length of the secondary base-line near Spring-green, Sauk County, Wisconsin, in 1878."

The atlas of plates belonging to this volume contains nine maps of the "Lead-bearing Crevices" of the Lead-region, and two illustrating the Triangulation of the Geodetic Survey.

An Index to the Palæontology, and a general index to the volume, complete this large and valuable addition to geological knowledge, not only useful to the citizens of the State where it has been produced, but welcome to geologists all over the world.

An Elementary Treatise on Conic Sections. By CHARLES SMITH, M.A. London: Macmillan and Co. 1883. (Pp. xi+352.)
An Elementary Treatise on Solid Geometry. Same Author and Publishers. 1884. (Pp. xv+230.)

WE have read this *second* edition of the 'Conics' as carefully as we read the first, and rise from the perusal with an enhanced opinion of its suitability as a text-book for College and School Students, in fact for all who wish to get an accurate and extensive acquaintance with this branch of mathematics. The text is very lucidly written, all the useful properties of the sections are clearly put, and the reader gets a full insight into the elegances of a very fascinating subject. Few students will need to carry their investigations further; and if they do require to advance, they will find Mr. Smith's book a capital preparation for such advanced treatises as that by Dr. Salmon.

The text, we may further remark, is very free from typographical errors; nor have we noted any mistakes of moment in the numerous exercises, many of which we have had occasion to work out. An inaccurately drawn figure which had place in the first edition is now replaced by an accurately drawn one. In addition to careful revision numerous additions have been made, more especially to the chapter on Involution, and to the final one on Reciprocal Polars and Projections.

Inspirited by the success of his first venture, Mr. Smith has ventured to send forth a second work, viz. one on Solid Geometry. We have formed much the same opinion on this work as we have expressed above: it appears to us to be written on the same lines and to possess the same good qualities. It is a very good elementary text-book, and can, we believe, be safely recommended as fit for the purpose for which the author has written it. The usual parts, of a large subject, which are considered as elementary are discussed in twelve chapters; and the only novelty in detail is perhaps the very early stage at which the discussion of the different surfaces represented by the general equation of the second degree (quadrics) takes place. We consider that this discussion is well done, and not at all likely to be too difficult for the beginner to master.

There are numerous exercises, worked out and unworked, and theorems due to Chasles and others are established. We commend the 'Solid Geometry' as a fitting sequel and complement to the 'Conics.'

An Elementary Treatise on the Differential Calculus, containing the theory of Plane Curves, with numerous examples. By BENJAMIN WILLIAMSON, *M.A., F.R.S.* London: Longmans. 1884. (Pp. xvi + 454.)

MR. WILLIAMSON'S works certainly meet the wants of a large class of students. His treatise on the Integral Calculus has reached a fourth edition, and the present work, an elder child, is now in its fifth edition. As time rolls on, so come the announcements of a new edition of one or the other work; and, as with the human offspring so with these, increase of age brings increase in size and knowledge. Mr. Williamson does not rest satisfied with so much good work achieved, but his motto is "onward," and so of the present treatise we can say "vires acquirit eundo."

Our author is ever careful to inform his readers that his book is principally intended for the use of beginners, but we fancy that in time he will leave little untouched that may concern the most advanced students. It would be now out of place to discuss such a work as this, upon which the world of mathematical students has stamped so clearly its "Imprimatur." It is for us only to wish "more power" to the able author, and trust that he will meet with like success in those new pastures in which, we learn, he is now expatiating—we allude to his forthcoming treatise on Dynamics.

We may note that the chapter on Roulettes and on the Envelope of any Curve carried by a rolling Curve is put more shipshape than in some of the earlier editions; that there is a full account of the Cartesian oval, a direction in which our author has done much good work; and, to crown all, the "latest novelty" is a short account of the Determinant functions yclept Jacobians—of which we expect to hear more in the 'Dynamics.' We wish Mr. William-son's treatise a "bon voyage."

LIII. *Intelligence and Miscellaneous Articles.*

DETERMINATION OF THE WAVE-LENGTHS OF THE PRINCIPAL LINES AND BANDS IN THE INFRA-RED PORTION OF THE SOLAR SPECTRUM. NOTE BY M. HENRI BECQUEREL.

IN a recent communication to the Académie des Sciences[*] on the lines in the infra-red part of the spectrum formed by incandescent metallic vapours, I had occasion to point out some corrections which I had been led to make in the numbers adopted in a previous research[†] for the wave-lengths of several lines and bands in the solar spectrum. I now give a *résumé* of my new determinations of the wave-lengths of the principal lines and bands in the infra-red portion of the solar spectrum.

The infra-red portion of the solar spectrum, from the group A

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[*] *Comptes Rendus,* August 25, 1884; Phil. Mag. October, p. 386.
[†] *Annales de Chimie et de Physique,* 5e série, t. xxx. p. 5.

to the extreme end of the visible part, shows, among other things, big absorption-bands. The two more-refrangible ones have already been split up into groups of bands and very fine lines; and it is probable that a more complete investigation would lead to a similar result for the two others. In my former researches I indicated these bands, starting from A, by the letters A′, A″, A‴, and A^IV.

The bands A′, A″, A‴ appear to have been observed by most physicists who have examined the infra-red region of the solar spectrum by thermoscopic methods, notably by J. Herschel, Fizeau and Foucault, Desains, and Lamansky. The same bands were observed by my father in 1866 by applying methods relating to phosphorescence; but the values (varying considerably among themselves) which different physicists have obtained for the wave-lengths of these rays do not allow of the identification, with any certainty, of the results of their researches. In 1847 Fizeau gave the number 0·001445 millim. for the wave-length of a band which appears to be the band A‴. On the other hand, my father obtained for this same band, by the phosphorographic method, numbers varying between 0·001400 and 0·001200 millim., and gave the number 0·001220 millim. for its most-refrangible border. It was therefore necessary to determine these wave-lengths directly by using a grating.

In 1879 Capt. Abney prepared a very beautiful map of the infrared portion of the normal spectrum; it was obtained by photography, and extended to about the wave-length 0·000980 millim. In my previous researches I was enabled, by the application of phosphorescence, to measure, in the diffraction-spectrum of a grating, to about 0·001000 millim.; but the feeble brilliancy of the spectra did not permit of my going further, and I adopted the number 0·001220 millim. for the most-refrangible border of the band A‴ which can be easily observed in the spectrum formed by a prism. The numbers above 0·001000 millim., published in the paper cited above, were obtained by means of an interpolation based upon this assumption.

In a memoir published in 1883 Mr. Langley deduces the wavelengths of the bands A′, A″, A‴, A^IV from their position in the spectrum formed by a prism by an ingenious method of graduation of his spectrobolometer; and the numbers obtained by him, starting from 0·001000 millim., differed considerably from those given by our hypothetical interpolation. I then proposed to make these determinations again, by throwing the diffraction-spectra obtained by a grating on phosphorescent substances considerably more sensible for infra-red rays than those which were at my disposal during my former researches. These substances have allowed of my measuring, with a sufficiently near approximation, the wave-lengths of the bands in question, as well as several of the finer lines; the numbers given by these experiments are near enough to those obtained by Mr. Langley with his bolometer, but the delicacy of the method of observation used by me is much greater.

The solar rays, concentrated upon a narrow slit, in the focus of a

collimator were made to fall upon a beautiful grating, ruled on metal by Mr. Rutherfurd, which M. Mascart was kind enough to lend me. The rays, brought to convergence by a lens, then traversed a bisulphide-of-carbon prism, of which the edges were at right angles to those of the slit and the lines of the grating, and formed upon the phosphorescent substance a series of oblique spectra, in which the rays of spectra of different orders were in juxtaposition and not superposed. The slit was sufficiently narrow to allow of distinctly seeing the principal lines of the luminous spectrum; and on comparing the position of the lines and bands in the infra-red part of the first spectrum with those of the known lines in the luminous part of the spectra of second and third order, their wave-length was obtained with an approximation, which depended only on the accuracy of the scale-reading.

The following Table contains the numbers obtained for the principal lines and bands. These numbers appear exact to within one or two millimetres, and may be substituted for those which have been given in the publications of my previous researches.

Wave-lengths of the principal lines and bands in the infra-red part of the solar spectrum, expressed in millionths of a millimetre.

700·4. A.
771.
783.
791 to 796.
804.
819. (Sodium).
830.
844.
858 to 862. Corresponds to a calcium group.
876.
898 to 900. (Magnesium.)
917 to 920. Band or group of lines.
934 to 945. ⎫
950 to 965. ⎬ A′. Group of lines and bands very near to one
968. ⎭ another.
992.
1025.
1069 to 1075.
1115 to 1119. ⎫ A″. Group of two bands which appear to be
1132 to 1142. ⎭ those indicated by Capt. Abney as ϕ_1 and ϕ_2.
1142. (Sodium.)
1200. (Magnesium,)
1254.
1354 to 1400. A‴. { Border distinct from 1351. Appears to
be the band named ψ by Abney.
1440. Feeble band.
1510 to 1560. Group of bands.
1800 to 1880. A^{IV}. { Approximate numbers. This band has
been called Ω by Mr. Langley.

The above results show that the phosphorographic method permits, when the phosphorescent substances are properly chosen, of the investigation of the infra-red part of the spectrum as far as thermoscopic and further than chemical methods.   This method has, further, an advantage that the others do not possess, namely that of giving a complete image, at one time, of the part which is to be studied.—*Comptes Rendus*, September 1, 1884.

INVESTIGATIONS ON RADIANT HEAT.   BY H. SCHNEEBELI.

In vol. lxxxiv. of Poggendorff's *Annalen*, p. 411 *et seqq.*, Svanberg describes a simple and very sensitive method for investigating radiant heat.

My object in the following experiments was to test the accuracy and capability of this method, and at the same time to solve experimentally some questions in radiant heat by its means.

Langley and Baur have in recent times used Svanberg's method to decide certain questions which present themselves in radiant heat, and have described arrangements for adapting the method to the various objects.

The arrangement which I chose in my experiments is the following :—

A grating of thin tinfoil blackened by platinum chloride and enclosed in a box with movable lid formed the resistance to be irradiated.   A Daniell's element was the electromotive force, and the mirror-galvanometer in the bridge was adjusted with such delicacy that a displacement of the contact-key of 1 millim. produced a deflection of some hundred divisions.   The resistance in the circuit in which was the battery was kept constant by an intercalated rheochord, and the current-strength was continually controlled.

Various circumstances led me to investigate the radiation in the following manner :—the tinfoil grating was exposed to radiation for ten seconds, the current was then closed, and the deflection read off.   The slide was of course so arranged beforehand that, on closing and opening before the radiation, the needle was at rest.

There is an evil in the method, which I will at once mention, that the small current in the bridge never continues for long ; so that even with a careful protection of the sensitive parts of the current there is no guarantee that during the ten seconds in which the radiation continued there is a null current even when the temperature of the grating is unaltered.   It seemed undesirable to use a shorter time for radiation, since the temperature of the grating is a function of the time, and increases very rapidly with the time, especially in the beginning, and thus slight inaccuracies in the time of exposure would produce great errors.   The following numbers show this :—

| Time of irradiation .... | 2 | 5 | 10 | 15 | 20 seconds. |
| Deflection .... | 270 | 300 | 321 | 328 | 331 |

Absorption of Radiant Heat in Glass.

The absorption of the rays which proceeded from an ignited platinum foil was first examined in various kinds of glass. The platinum foil was in the non-luminous flame of a Bunsen's burner. The glass plates were chosen from pieces of window-glass and of plates of electrical machines, and had approximately the same thickness, for only in this case can the absorptions of the various plates be compared with each other.

The coefficient of absorption was calculated from the formula

$$J = J_0 e^{-kx}, \quad \text{to} \quad k = \frac{\log \frac{J_0}{J}}{x},$$

in which

x is the thickness of the absorbing plate,

J_0 the intensity of the incident,

J that of the transmitted rays.

The following table gives a representation of the absorption in the disks chosen :—

Thickness of the disks.	J_0.	J.	k.
millim.			
1·8	142·9	70·0	0·396
1·8	143·0	69·5	0·400
1·75	142·5	70·5	0·401
1·70	142·5	71·5	0·405
1·90	142·0	68·5	0·383

The table shows that the glass plates investigated possess a pretty equal absorptive power ; the larger variations which occur with No. 4 and No. 5 are easily explained from the different thickness of the two plates. It results from the following that the coefficient of absorption greatly decreases with increased thickness.

The question was further investigated, How is the coefficient of absorption altered at various depths of the irradiated layer of glass ? The following table elucidates this : δ is the thickness of the glass plate already traversed before the absorption in the glass plate of 1·75 millim. thickness is measured. A luminous gas-flame served as a radiating source.

δ, thickness of the layer of glass already traversed.	Thickness of the absorbing glass plate.	k.
millim.	millim.	
0	1·75	0·419
1·85	1·75	0·207
5	1·75	0·150
10	1·75	0·084

The absorptive capacity of gas was examined for radiant sources of various temperatures. The number for the temperature 100° can only be considered approximate.

Temperature of the radiating body.	Thickness of the absorbing glass plate.	k.
	millim.	
100°	1·75	2·4
250	1·75	1·47
about 1000	1·75	0·42

Investigation of the Radiation of a Swan's Lamp at various Temperatures.

The radiation of a small Swan's lamp (resistance when cold 80 ohms) was also determined when heated by currents of various strengths, from a red heat to a white heat. The currents used were furnished by a Gramme machine, and were measured by means of a differential galvanometer for strong currents. The readings were made by the aid of mirror, scale, and telescope. The numbers in the following table give the readings, and therefore the relative strengths of the current. At the same time the luminosity of the lamp corresponding to the different strengths of current was determined. The following tables were thus obtained :—

I. Series.		
Strength of current.	Total radiation.	Optical radiation in candles.
44·5	87·0	0·12
48·8	97·0	0·25
57·0	158·0	0·70
67·0	195	1·85
75·0	250	5·4
88·2	348	17·5

II. Series.		
Strength of current.	Total radiation.	Optical radiation in candles.
48·0	102·0	0·3
76·2	254·0	5·5
94·2	392·0	24·0

Both series show very clearly how enormously the emission of light increases with increasing temperature.

The following considerations show that there is a simple relation between strength of current and total emission. The thermal equilibrium of the lamp is defined for each strength of current by the fact that the quantity of heat produced by the current in the lamp is equal to that given out. Hence for each strength of current J the following relation holds—

$$J^2W = C \cdot S,$$

where

W is the resistance of the carbon filament at the temperature in question ;

S the radiant energy sent out by the lamp ; and

C a constant.

From the above equation we get

$$\frac{J^2W}{S} = C.$$

If W, the resistance of the carbon filament for the temperatures here in question (900–1500°), were constant, the quotient must be a constant,

$$\frac{J^2}{S}.$$

The following values are obtained for these quotients for the strengths of currents :—

| J ...... | 44·5 | 48·8 | 57·0 | 67·0 | 75·0 | 88·2 | 48·0 | 76·2 | 94·2 |
| J^2/S ... | 22·8 | 24·5 | 20·7 | 23·0 | 22·5 | 22·4 | 22·6 | 22·8 | 22·6 |

Such deviations as occur in two experiments are to be ascribed to variations in the current which occur during the observation of the total radiation. It follows, therefore, from the table that the resistance of the carbon filament from about red heat to white heat is, so to speak, independent of the temperature. This seems to be the case for the coefficient of absorption of the glass globe of the lamp. I may take the opportunity of remarking that ordi-

nary amorphous charcoal is in general as bad a conductor as paraffin, but at a red heat is a very good conductor.—Wiedemann's *Annalen*, No. 7, 1884, p. 430.

ON MR. MOON'S METHOD OF CALCULATING THE RATIO OF THE TWO SPECIFIC HEATS OF GASES.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

The paper by Mr. Moon in the last number of the Phil. Mag. (p. 372) is an instructive example of the evil of an indistinct and foggy style of writing. Had he set himself to think what was the real gist of his argument, he could not have failed to perceive that his method of calculating γ is an old and well-known one, taught to all junior students of thermodynamics, and first virtually suggested by Mayer.

The argument, put concisely but quite fully, is as follows:—More energy is needed to warm gas at constant pressure than at constant volume, because of the work done in expanding. Equating the extra energy expended per gramme of gas to the external work done (as Joule and Thomson have entitled us to do), we get

$$J(c'-c)d\mathrm{T}=pdv\,;$$

but the fundamental property of a gas, $pv=R\mathrm{T}$, combined with the fact that the above change of volume occurred under constant pressure, gives

$$pdv=Rd\mathrm{T},$$

whence

$$c'-c=\frac{\mathrm{R}}{\mathrm{J}}.$$

Putting into this equation the numerical values selected by Mr. Moon for c', J, and R, $\dfrac{c'}{c}$ will come out equal to 1·41095, as he correctly reckons.

Any one referring to Mr. Moon's paper will perceive how elaborately he has involved this simple matter until it has become laborious to disentangle his meaning.

The difficulty of reading and appreciating what is good and new in work would be greatly diminished if authors would more frequently take pains to express themselves as clearly and distinctly as possible. Your obedient servant,

Univ. Coll., Liverpool, OLIVER J. LODGE.
Oct. 13, 1884.

LIV. *On the Changes produced in the Molecular Condition of Iron by Heating to Redness and Cooling.* By CARL FROMME[*].

SOME years ago, upon the publication of some magnetic experiments[†], I made a short communication upon the change in density which steel undergoes upon hardening, and subsequently added to the fuller description [‡] of the same experiments, in these *Annalen*, a series of observations made to determine the distribution of density in the interior of a hardened steel bar. The general applicability of one of the former results has recently been called in question by observations of H. Meyer[§]. These observations show an increase in density upon hardening for one ("drawn soft bright steel") of three kinds of steel examined, whilst the other two kinds ("best bright English cast steel" and "polished English steel") showed the decrease which alone I had observed[‖]. I have therefore made new experiments upon these phenomena of change of density upon hardening, and endeavoured to obtain a nearer insight into the reasons of these phenomena by extending the observations to the different modifications of iron, from pure electrolytic iron free from carbon to the more highly carbonaceous cast iron.

The question of the distribution of density in a hardened steel bar had been far from solved by the single series of obser-

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[*] Translated from Wiedemann's *Annalen*, No. 7 (1884).
[†] *Gött. Nachr.* 1876, pp. 157–168.
[‡] *Wied. Ann.* viii. pp. 352–356 (1879); Phil. Mag. [5] viii. p. 421 (1879).
[§] H. Meyer, Wied. *Ann.* xviii. p. 233 (1883).
[‖] There is an older observation of Rinmann (in his *Geschichte des Eisens*, German translation by Karsten), according to which Styrian steel experienced an increase in density of from 7·782 to 7·822 upon hardening.

vations which I had published ; on the contrary, their result had been so remarkable and unexpected that further experiments were much to be desired. Since I have not in the mean time become acquainted with investigations on this subject, I offer now a small contribution to the solution of the question.

1. *On the Change in Density produced by Tempering Iron.*

The following materials were employed :—

(a) Iron wire 1·4 millim. thick.

(b) Iron wire 0·5 millim. thick, obtained by drawing out the wire (a).

(c) Iron wire 0·3 millim. thick.

(d) Steel wire 0·7 millim. thick.

(e) Steel wire 0·4 millim. thick. (d) and (e) were from the same works in Birmingham, and were called "patent steel music-wire."

(f) Cylindrical steel rod 5·5 millim. thick, 30 millim. long.

(g) Electrolytic iron in small pieces, deposited from a solution of ferrous sulphate. Thickness about 0·1 millim.

(h) Electrolytic iron deposited from a solution of ferric chloride. Three small pieces were cut from a large piece and tested separately. Mean thickness of the large piece 0·14 millim.

(i) Cast iron in the form of a cylinder, 18 millim. long and 7 millim. thick.

(k) Cast iron in the form of a plate (20 : 10 : 5 millim.).

(l) Wrought iron in the form of a cylinder 25 millim. long and 5·6 millim. thick.

(m) White pig-iron in small pieces, such as could be obtained from a larger piece by breaking it up with a hammer.

For determination of density, a Geissler's pycnometer was employed, except for (h) and (k), the densities of which were determined with the hydrostatic balance. The metal was heated in the flame of the Bunsen burner or in the blowpipe-flame.

When slow cooling was desired the pieces of metal were allowed to cool in the bright flame and above it, whilst rapid cooling was attained by plunging the hot body into water of 10° or 15°. The coating of oxide was removed before each determination. The wires were examined by cutting off pieces suitable to the height of the vessel of the pycnometer, of about 4 centim. long, and testing a number together (thirty in the case of the thinnest wires).

Each specimen was first heated and cooled slowly, and then its density δ_l measured ; then it was heated again and cooled rapidly, and its density δ_r determined. Thus determinations of δ_l and δ_r alternated with each other, often repeatedly. Table I. exhibits all the observations brought together.

TABLE I.

Designation of material.	Slowly cooled. $\delta l.$	Rapidly cooled. $\delta r.$	$\delta r - \delta l.$		$\delta r - \delta l.$ Mean.
a	7·4772 4522 4495 4384	7·4642 4572 4554 4367	−0·0005 +0·0084 +0·0068 +0·0068	+0·0115 +0·0076	+0·007
b	7·2830 2370 2064 1925	7·2585 1937 1977 1587	−0·0015 −0·0109 −0·0280 −0·0107	−0·0017 −0·0143	−0·011
c	7·7585 7319 7022	7·7549 7449 7237	+0·0097 +0·0180 +0·0279	+0·0321	+0·022
c ...... (a second wire)	7·7571 7422 7240	7·7794 7879 7534	+0·0298 +0·0414 +0·0548	+0·0466	+0·043
d	7·7954 7754	7·7240 6874	−0·0614 −0·0697	....	−0·066
e	7·7742 7602	7·7119 6834	−0·0553 −0·0626	....	−0·059
f	7·7970	7·7210	−0·0760	......	−0·076
g	7·5682	7·5689	+0·0007	......	+0·001
h_1	...... 7·6574 6669 6714	7·6334 6334 6656 6892	−0·0240 0·0287 −0·0174 −0·0035	+0·0060	−0·013
h_2	...... 7·7026 6960 7020	7·6927 6912 7044 6888	−0·0107 −0·0081 +0·0018 +0·0054	−0·0054	−0·003
h_3	...... 7·7110 6937 6989	7·7047 6867 7072 6978	−0·0153 −0·0156 +0·0032 +0·0109	+0·0036	−0·003
i	7·0412 7·0152 6·9989	7·0137 7·0052 6·9919	−0·0145 −0·0058 −0·0018	−0·0004	−0·006
k	7·1465 1402 1345 1266 1097 1024 0986 0915	7·1384 1319 1297 1004 1029 1042 0887 0906	−0·0049 −0·0051 −0·0054 −0·0037 −0·0008 −0·0116 −0·0117 −0·0081	−0·0031 +0·0011 +0·0037 −0·0022 −0·0063 −0·0019	−0·005
l	7·6564 6444	7·6530 6344	+0·0026 −0·0007	....	+0·001
m	7·6320 5915	7·5539 5209	−0·0578 −0·0541	....	−0·056
m ...... (other pieces)	7·5754 5510	7·5097 4805	−0·0535 −0·0559	....	−0·055

The first point which strikes the eye upon examining this table is the decrease, often considerable, which is produced by repeated heating, in the density of all the kinds of iron, with the single exception of electrolytic iron.

The exception, presented by pure iron only [*], suggests the cause of the phenomenon ; it evidently is to be sought in the varying proportion of carbon contained in the material which will suffer change upon ignition. The total percentage of carbon may vary, as well as the proportion between combined carbon and graphite. It may be noted that none of the pieces were heated longer than necessary. The smallest value of the density is then often not reached after repeatedly heating. This continuous decrease in density made it necessary to combine the determinations suitably, before the question proposed as to the difference in density caused by rapid cooling and slow cooling could be answered. I have combined each measurement with that preceding and that following it, and thus obtained the numbers contained in the fourth column of Table I. The intermediate members of the series δ_l and δ_r have, however, more share in the formation of these differences than the terminal numbers. Nevertheless I have taken the simple arithmetical mean of all the differences to three places of decimals, since it does not depend upon a knowledge of the exact values of $\delta_r - \delta_l$.

If we now compare with each other the mean values contained in the last column, we find an increase in specific gravity upon rapid cooling only with the iron wires a and c, the electrolytic iron g, and the wrought iron l. We have, however, only one measurement of the electrolytic iron g, and the difference resulting from it lies within the limit of experimental error. For the wrought iron l we have two differential values; but they are of small magnitude and of different sign. Hence we may conclude that with the electrolytic iron (g) and with the wrought iron (l) the density is sensibly independent of the velocity with which the heated substance cools.

On the other hand, an increase in specific gravity after tempering is distinctly observed with the iron wires (a) and (c), and with the wires (e) it is even considerable.

All the other substances examined—that is to say, the iron wires, the steel wires (d) and (e), the steel bar (f), the electrolytic iron (h), the cast iron (grey pig-iron) (i) and (k), and, lastly, the white pig-iron (m)—all suffered a decrease in specific

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[*] With the piece h_1, on the contrary, the specific gravity increased upon repeated heating. To begin with, it was decidedly smaller than that of the other two pieces, but upon repeated heating became continually more nearly the same.

gravity upon tempering. This decrease is the greatest in the case of steel and white cast iron, smaller with the iron wire (c), and smallest with the cast iron and the electrolytic iron. But whilst this decrease in density is beyond doubt with all the kinds of steel examined, the iron wire, and the grey and white pig-iron, the mean values found for the electrolytic iron must be received with caution ; since, of the whole fifteen values of $\delta_r - \delta_l$, nine are positive and six negative. Hence I consider it not improbable that a larger number of measurements (which was not possible on account of the gradual diminution in the size of the piece) would give a mean value approaching zero. I therefore regard the existence of a difference in density of electrolytic iron, after slow cooling or rapid cooling, as not proved. The different varieties of iron are classified, as we know, according to the quantity of carbon they contain, which may be present either in the free condition or chemically combined ; for the percentage of carbon determines, if not exclusively yet to a great extent, the properties of any particular kind of iron. Hence I had no doubt that both the sign and magnitude of the change in density produced by tempering would be dependent upon the percentage of carbon. The observations indeed do not contradict this assumption, but they by no means determine the law of the connexion. It results from the measurements made with cast iron and with white pig-iron, that the change in density depends less upon the total percentage of carbon than upon the quantity of chemically combined carbon. For in the case of white pig-iron containing much combined carbon, the change was ten times as great as with grey pig-iron, in which the carbon was contained chiefly as graphite.

Whilst with white pig-iron and steel (substances containing the largest percentage of combined carbon) the density diminished upon tempering, it increased with the three kinds of iron wire examined—substances which contained only a small percentage of combined carbon. The third kind of iron wire, obtained by drawing down one of the first two kinds, behaved in the opposite way; which may possibly be explained by a change of free carbon into combined carbon, caused by the operation of drawing. If so, smaller quantities of chemically combined carbon in iron produce an increase in density, and larger quantities a decrease, when the red-hot wire is plunged into cold water.

This assumption does not appear to be negatived by the two observations, which alone, so far as I know, have shown an increase in density of steel upon tempering. For, according to a table given in Scheerer's *Metallurgie,* Styrian steel,

with which Rinmann experimented, contains only a small quantity of carbon; and the designation of the steel examined by H. Meyer as "soft" also points to a small percentage of carbon.

Whether the view which I have expressed, chiefly by way of surmise, is correct or not must be decided by more extended experiments, accompanied by analysis of the kinds of iron examined.

Mousson, in his *Lehrbuch der Physik*, has endeavoured to explain the change in density produced by tempering as purely mechanical, assuming that the initial cooling of the exterior prevents the interior portions from contracting, as they otherwise would do upon the fall of temperature.   Hence the exterior layers are left in a condition of forcible compression, and the interior in a condition of forcible extension.   Hence, according to Mousson, three things would follow :—first, an increased density and hardness of the superficial layers ; secondly, a diminished density and hardness of the interior ; and, thirdly, an increase in volume.

Let us for the present disregard the first two, and concern ourselves only with the third result.

This conclusion is in opposition to the results obtained with the iron wires (*a*) and (*c*), as well as the observations of Rinmann and Meyer.   Any such purely mechanical explanation of the processes involved in tempering can certainly not be maintained.   But, since Mousson's explanation takes no account of chemical changes during the process of tempering, and since it can be shown that such changes occur in iron containing carbon, it seemed possible that the above explanation might at least be applicable to pure iron ; and in fact pure iron does exhibit on the whole an increase of volume upon tempering.   But, as already pointed out, the mean values obtained cannot be considered decisive upon this point. I have further examined platinum, but did not succeed in showing any change in volume.

On this account I am of opinion that a change of volume, as a result of rapid cooling, only takes place with good conductors, such as the metals, if chemical changes occur at the same time.   On the other hand, I do not at all deny the possibility of such changes with substances of small conducting-power for heat, such as glass.

2. *On the Distribution of Density and Hardness in Tempered Steel.*

I have made experiments upon the distribution of density and hardness only with one kind of steel, that marked *f*.

Before describing these experiments, I wish to mention a few experiments made with other kinds of iron.

It is well known that no sharp distinction, depending only on percentage of carbon, can be drawn between wrought iron and steel. For the property of hardness characteristic of steel is dependent not only upon the quantity of carbon, but also upon the presence of traces of other metals; so that iron containing only about 0·5 per cent. of carbon, if it contains also other metals as impurities, may be hardened, and thus behaves like steel. Only when it contains still smaller quantities of carbon (less than 0·5 per cent.) can iron be indiscriminately characterized as soft iron, *i. e.* it acquires only slightly increased hardness by being suddenly cooled in cold water; and this increase is the less the smaller the percentage of carbon and other foreign substances. This is the usual view, and Karsten expresses himself to the same effect in his *Handbuch der Eisenhüttenkunde*, when he says, " It is characteristic of all kinds of bar-iron that their hardness is not perceptibly increased by being suddenly quenched in cold water."

My experiments entirely agree with this result : the varieties of iron wire (*b*) and (*c*) were found to be distinctly, but not considerably, harder after rapid cooling than when slowly cooled, since they offered more resistance to flexure. *The hardness has therefore no connexion with the simultaneous change in density*; since, whilst the density of (*b*) decreased, that of (*c*) increased. I was not able to obtain any definite result with the iron wire (*a*) on account of its greater thickness. The electrolytic iron was certainly not made harder by sudden cooling. Lastly, I have tested the cast iron, as well as the brittle white pig-iron, with the file, but without any certain result.

Lastly must be mentioned that platinum and copper do not appear to become harder by sudden cooling than by slow cooling. It appears, then, that the property possessed by metals of being hardened is associated with the commencement of a chemical change. In the case of iron it is chiefly carbon, which, when it is present in certain quantities, neither too great nor too small, undergoes chemical change upon sudden cooling, and is thus the cause of the hardening which takes place.

Five pieces were cut from a cylindrical rod of steel of 0·55 centim. diameter. Four of these of the same length (about 3 centim.) were heated and cooled quickly, (*a*) and (*b*) in water of 45°, (*c*) and (*d*) in water of 15°. The fifth piece (*e*) was only 2·3 centim. long. It was made red hot and allowed to cool gradually to the temperature of the room. After deter-

mining the densities of the pieces, they were placed in nitric
acid to which a little hydrochloric acid had been added, and
were allowed to be acted upon to a certain extent; then the
density was determined again; they were further acted upon
by the acid; and so on.

The action took place, on the whole, very regularly: the
bars retained their cylindrical form and smooth surface; two
of the pieces showed channels, but of very small depth.

The hydrostatic balance was employed for the determination
of density, except that the first ten observations with the
bar (*b*) were made with the previously mentioned pycnometer.
Table II. contains the results of the determination of density,
together with the absolute weights of the pieces.

TABLE II.

No. of obs.	*a.*		*b.*		*c.*		*d.*		*e.*	
	m.	*δ.*	*m.*	*δ.*	*m.*	*δ.*	*m.*	*δ.*	*m.*	*δ.*
1.	6·635	7·735	6·480	7·714	6·328	7·715	6·338	7·727	4·931	7·795
2.	624	734	462	703	245	704	248	718	856	790
3.	610	731	452	754	204	706	122	718	777	789
4.	596	733	402	754	142	706	005	713	670	794
5.	576	729	360	760	051	704	5·892	716	577	793
6.	538	731	321	758	5·946	698	784	716	508	792
7.	495	731	282	759	803	702	625	723	437	798
8.	474	731	229	757	332	700	531	718	343	791
9.	424	730	188	753	181	704	377	716	270	793
10.	349	732	154	758	4·868	696	278	715	177	789
11.	296	733	115	745	594	708	145	714	103	788
12.	241	731	072	747	297	705	026	704	3·999	791
13.	080	728	016	745	060	701	4·909	708	861	790
14.	018	735	5·974	743	3·778	697	772	704	771	787
15.	5·754	730	916	747	535	698	607	710	656	783
16.	587	735	857	739	202	710	391	710	590	786
17.	129	725	813	733	2·898	693	201	714	507	781
18.	4·630	728	756	735	...	...	3·973	705	395	789
19.	177	731	696	736	...	...	759	705	318	792
20.	3·645	735	649	739	...	...	559	700	216	795
21.	038	734	590	737	...	...	388	720	116	792
22.	2·747	733	527	736	...	...	237	715	2·987	794
23.	...	...	484	737	...	...	049	715	880	780
24.	...	...	435	736	...	...	2·882	708	...	...
25.	...	...	378	740	...	...	737	705	...	...
26.	...	...	321	737	...	...	...	...	...	...
27.	...	...	247	736	...	...	...	...	...	...
28.	...	...	176	735	...	...	...	...	...	...
29.	...	...	083	736	...	...	...	...	...	...
30.	...	...	4·998	734	...	...	...	...	...	...
31.	...	...	660	735	...	...	...	...	...	...

The density of the bar (*a*) thus remained nearly constant
throughout the process of dissolving away. It was almost

always somewhat smaller (at most by 0·007) than at first, and only reached the initial value three times, *i. e.* the mean density of the unattacked and newly tempered bar ; on the average it was smaller by 0·004. With the bar (*b*) the density at first diminished rapidly, then increased, and then gradually sank with small variations to a constant value, greater than the initial value.

With the other two bars (*c*) and (*d*), which were cooled in colder water, the density alternately diminished and increased, and the changes took place much in the same way, a maximum or minimum occurring about the same densities of the bar. In both cases the density remained lower than the initial value ; on the average it was about 0·015 less.

Of these four series of observations the second leads to very remarkable results. If we calculate the densities of the layers removed between the first and second observation, and between the second and third observation, we find the values to be 16 and 2. The thickness of each of the two layers would be about 0·002 millim.

Although, on account of the smallness of the quantities dissolved off, these numbers may be affected by errors of relatively large magnitude, yet, unless we suppose gross errors of observation to exist, which I do not consider to be probable, the fact remains that between an external dense layer and a central portion of nearly uniform density there existed a layer of extraordinarily small density. Apart from this peculiar condition of the surface, the distribution of density is quite regular—the density decreases until it reaches a constant value. Consequently we have a dense envelope enclosing a less dense kernel.

The first series of observations, which relate to a bar tempered in warm water, shows an extraordinarily small difference in density. The greatest difference between any two observations amounts to seven in the third decimal place, which may certainly be attributed to accidental want of homogeneity. From the fact that the density becomes less upon the whole, we may certainly conclude that this bar must have possessed a density decreasing, with small variations, from outside towards the interior.

The same conclusion follows from the measurements made with the two pieces (*c*) and (*d*), which were tempered in cold water. With them, however, the difference between the density of the exterior layer and the interior is much greater than with the bar (*a*), but the irregularities in the distribution of density are also much greater.

I have calculated the densities of the layers, dissolved away

between two observations, giving a relative maximum or minimum. Table III. A contains the results of this calculation for the bar (d), as well as the mean density of the layers dissolved off up to the observation in question, and the mean density of the portion left.

TABLE III. A.

Number of observation.	δ_1. Density of layer removed between two observations.	δ_2. Density of the portions removed between the first observation and one of the subsequent ones.	δ_3. Density of the part of the bar unattacked.
1.	...	...	...
4.	7·98	7·98	7·71
7.	7·58	7·76	7·72
13.	7·88	7·82	7·70
17.	7·65	7·75	7·71
20.	7·79	9·79	7·70
21.	7·31	7·74	7·72
26.	7·76	7·74	7·71

The values of δ_1 show that there are layers of greater and smaller density, alternating with each other; those of δ_2 taken together with those of δ_3 show that the density decreases from the outside towards the centre, since the density of the part dissolved away always exceeds that of the remaining portion.

The slowly cooled bar (e) was examined to see if the alternating layers of denser and less dense metal were produced by the sudden cooling.

Table III. B relates to the rod (e); δ_1, δ_2, δ_3 have the same signification as in Table III A.

TABLE III. B.

Number of observation.	δ_1.	δ_2.	δ_3.
1.	...	...	...
3.	7·93	7·93	7·79
7.	7·70	7·77	7·80
11.	7·89	7·82	7·78
17.	7·75	7·79	7·78
20.	7·64	7·76	7·79
23.	7·92	7·79	7·78

We find, then, the slowly cooled bar possesses exactly similar variations in density as that cooled quickly in cold

water ; whence it follows that they are not produced by the sudden cooling, but are to be regarded as indicating original want of homogeneity in the bar.

A comparison of δ_2 with δ_3 shows that the density of the portion of the bar dissolved away is only twice decidedly greater than that of the remaining portion. There is therefore no decrease of density from the surface towards the axis in the slowly cooled bar.

The foregoing experiments, taken together, therefore confirm the common belief that, in consequence of rapid cooling, a distribution of density results, in which the density decreases from the outside towards the centre.

I have so far spoken only of the distribution of density in a tempered steel bar. According to the usual view, supported also by Mousson, not only the density, but also the hardness becomes smaller from the outside towards the centre, so that a harder shell encloses a softer kernel.

During the gradual dissolving of the bars by acid, they were tested with a good file as to their hardness. All four bars showed themselves so hard through the entire substance —they were dissolved away so far that the remainder was only 1·5 millim. thick—that they could not be scratched by the file. The slowly cooled bar, on the contrary, was throughout very soft.

Although we must admit the possibility of the tempered bar being harder outside than inside, yet the assumption of a softer kernel enclosed by a harder shell is not proved, and would probably not be found to be the case in all steel bars of thickness less than those employed in these experiments.

Such bars therefore, whether cooled in warm or in cold water, must be regarded as homogeneous in respect of hardness.

It must remain for further experiments to decide whether this result holds good for still thicker bars, or how thick the bar may be, so that the interior shall remain soft in spite of tempering.

If we take this result together with that of the experiments upon density, we see that in tempered steel hardness and density do not go together, but that smaller hardness may correspond to greater density, and *vice versâ.* For, according to Table III. A, of seven layers removed from a steel bar four possessed a density considerably smaller than the mean density of the slowly cooled soft bar, and yet were quite hard. The same result is arrived at by observing that the outer layer of the bar (*e*), according to Table III. B, possessed a calculated density of 7·93, and yet, in spite of the high density, was perfectly soft.

Of the three consequences of a purely mechanical explanation of the processes involved in the hardening of steel by sudden cooling, that which relates to the distribution of density has been shown to be correct ; the second, concerning the distribution of hardness, could not be demonstrated absolutely, although it is not to be concluded that it may not be correct for thicker bars ; and the third, which requires an increase of volume produced by sudden cooling, corresponds, it is true, to the behaviour of most kinds of steel, but is strikingly contradicted by the behaviour of other kinds. The mechanical explanation in question assumes, lastly, a parallelism between density and hardness, since it explains an increase in hardness by an increase in density. We have seen, however, that density and hardness by no means increase or decrease together.

Hence we arrive at the conclusion that in the tempering of a steel bar, besides the mechanical, purely physical, process of sudden contraction, another change also, of chemical nature, takes place. This consists in a combination between the free carbon and the iron.

Barus* arrived at the same result some years ago, by means of other experiments and considerations. He considers the combination of carbon as the chief reason of hardness, which may, however, be somewhat modified by the mechanical process.

If, however, we inquire further into the reason of the combination of the carbon, we easily see that the reason can only be sought in the mechanical process, which appears then as the primary cause of hardening. It appears to me that it is essentially great pressures, produced by the sudden contraction of the red-hot steel plunged into cold water, which bring about the combination of the carbon and the iron.

This same idea has been already expressed in a paper published twenty years ago by Caron†. Experiments are there described which are concerned with the behaviour of suddenly cooled steel, of hammered steel, and of slowly cooled steel when treated with acids. The result obtained was that the residue of carbon was inappreciable in the first case, more considerable in the second case, and largest in the third case. Caron concludes from this that the steel hardened by sudden cooling contained its carbon almost altogether chemically, and that the change produced in the most complete manner by sudden cooling may be, partially at least, brought about by

* Wied. *Ann.* vii. p. 383 (1879).
† *Comptes Rendus,* lvi. pp. 45, 211 (1863).

hammering. The reason of the combination of the carbon would, however, be the same in both cases—namely, the closer approximation of the molecules produced by pressure; and the smaller effect produced by hammering is explained by the fact that, in the first place, upon hammering the approximation takes place in one direction only, but upon cooling in all directions at once, and that, secondly, the pressures exerted are less intense than those produced by cooling.

If this view of the cause of the hardening of steel produced by sudden cooling be correct, it must also be possible to harden steel by allowing it to cool slowly from the red-hot condition, but so that during the cooling it is exposed to high pressure. Steel thus treated ought, then, like tempered steel, to contain more combined carbon, and to be hard. In fact, according to Clémandot [*] and Lan [†], both of these conclusions are verified by experiment.

LV. *Geometrical Methods in the Theory of Refraction at one or more Spherical Surfaces.* By JAMES LOUDON, *University College, Toronto* [‡].

[Plate X.]

1. IN cases of reflection or refraction at a spherical surface, or a combination of spherical surfaces, or lenses, if F, F′ be the primary and secondary principal foci of the surface, lens, or combination, and (P, P′), (R, R′) pairs of conjugate points, it is known (§ 6) that

$$\frac{f}{p} + \frac{f'}{p'} = 1, \quad \cdots \quad \cdots \quad (1)$$

where $f = RF$, $p = RP$, $f' = R'F'$, $p' = R'P'$; and where the positive direction from R for f and p is opposite to, whilst that from R′ for f' and p' is the same as, the direction of the incident pencil.

Now since the relation (1) expresses the condition that the line $\frac{x}{p} + \frac{y}{p'} = 1$ passes through the point (f, f'), it follows that if the coincident lines FRR′F′, FR′RF′ be separated so that R on the first axis coincides with R′ on the second, the line joining P on the former to P′ on the latter will always pass through the fixed point (f, f'). Hence we derive a geome-

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[*] *Comptes Rendus*, xciv. p. 703 (1882); xcv. p. 587 (1882).
[†] *Ibid.* xciv. p. 952 (1882).
[‡] Communicated by the Author.

trical method for determining the point conjugate to any given one.

The points R, R′ from which distances are measured, it is to be observed, are any two conjugate points, such, for example, as the principal points, or nodal points ; and they may in particular cases coincide when they are self-conjugate.

It is proposed in the following paper to employ the method indicated chiefly in discussing certain propositions in the theory of thick lenses.

I.

2. In the case of refraction at a single spherical surface,

$$\frac{f}{p} + \frac{f'}{p'} = 1,$$

where f, f' are the distances of the primary and secondary principal foci F, F′, and p, p' the distances of the object and image P, P′ from A the point where the principal axis meets the sphere.

Let the standard case be that of refraction into a denser medium whose surface is convex, the direction of the light being from left to right. Then drawing axes AF, AF′, and taking the point X(f, f'), as in fig. 1 (Plate X.), we see that the point conjugate to P on one axis is the intersection of PX with the other.

It appears from the figure that A is a self-conjugate point, as also O, FO being equal to FX.

3. From similar triangles PFX, XF′P′, it is immediately seen that

$$f f' = d d',$$

where PF $= d$, P′F′ $= d'$.

If the rule of signs (§ 1) be applied to the measurement of d, d' on the two axes, it is to be observed that they are of the same sign, both being negative, for example, in fig. 1.

4. If P, P′ are conjugate points, as also Q, Q′, then drawing PXP′ QXQ′, as in fig. 1, we have

$$d d' = (d + \mathrm{PQ})(d' - \mathrm{P'Q'}),$$

which reduces at once to

$$-\frac{d}{\mathrm{PQ}} + \frac{d'}{\mathrm{P'Q'}} = 1.$$

This is of the form

$$\frac{d}{\mathrm{D}} + \frac{d'}{\mathrm{D'}} = 1; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the distances d, D are measured from P, and d', D′

from its conjugate P′, the rule of signs being that already referred to (§ 1).

5. Fig. 2 exhibits the construction adapted to formula (2). P in one axis coincides with its conjugate P′ in the other, and the line joining any other two conjugate points Q, Q′ on the two axes passes through the point (d, d').

If the origin be the self-conjugate point O, the centre of the sphere, the relation (2) becomes

$$\frac{f'}{p} + \frac{f}{p'} = 1;$$

where (fig. 3)

$$OF = f', \quad OP = p, \text{ &c.}$$

As in § 3, we have

$$dd' = f'f.$$

6. In the following proposition, which, in the form given, is due to Helmholtz (vide *Optique Physiologique*, p. 72), I have changed his notation and employed the rule of signs (§ 1), in order to exhibit the result of the elimination in a symmetrical form.

Let there be any number of spherical refracting surfaces whose principal foci are (F_1, F'_1), (F_2, F'_2), &c., and which cut the common principal axis in A, B, C,... Let (R_0, R_1), (R_1, R_2)... be pairs of conjugate points such that $R_0F_1 = d_0$, $R_1F'_1 = d'_1$,... In like manner let (P_0, P_1), (P_1, P_2)... be any other set of conjugate points, such that $R_0P_0 = p_0$, $R_1P_1 = p'_1$,... Then, by § 4,

$$\frac{d_0}{p_0} + \frac{d'_1}{p'_1} = 1,$$

$$\frac{d_1}{p_1} + \frac{d'_2}{p'_2} = 1, \text{ &c.}$$

Also by the rule of signs (§ 1) we have $p_1 = -p'_1$, $p_2 = -p'_2$,... Hence, on eliminating these quantities, the position of P_n, the point conjugate to P_0 with reference to the system, is determined from an equation of the form

$$\frac{f}{p_0} + \frac{f'}{p'_n} = 1, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $f = R_0F$, $f' = R_nF'$; F, F′ being the principal foci of the system.

The values of $\dfrac{f}{d_0}$ for 2, 3, 4, ... refractions are, respectively,

$$\frac{d_1}{d_1 + d'_1}, \quad \frac{d_1 d_2}{d_1 d_2 + d'_1 d_2 + d'_1 d'_2}, \quad \frac{d_1 d_2 d_3}{d_1 d_2 d_3 + d'_1 d_2 d_3 + d'_1 d'_2 d_3 + d'_1 d'_2 d'_3} \cdots$$

and the corresponding values for $\dfrac{f'}{d'_2}, \dfrac{f'}{d'_3}, \dfrac{f'}{d'_4}, \ldots$ are

$$\frac{d'_1}{d_1 + d'_1}, \quad \frac{d'_1 d'_2}{d_1 d_2 + \ldots}, \quad \frac{d'_1 d'_2 d'_3}{d_1 d_2 d_3 + \ldots}, \ldots$$

7. The construction of § 5 (fig. 2) applies to equation (3); and from the figure we at once deduce, as in §§ 3 and 4, the general relations for any system

$$dd' = ff', \quad \frac{d}{D} + \frac{d'}{D'} = 1.$$

The latter, it may be observed, also follows from (3), since R_0, R_n are *any* conjugate points.

8. The principal foci F, F' of a system of two surfaces S_1, S_2 constituting a lens may be found as follows:—

Let (F_1, F'_1), (F_2, F'_2) be the principal foci of S_1 and S_2, which cut the principal axis in A, B respectively, so that $AF_1 = f_1$, $AF'_1 = f'_1$, … In fig. 4 take the point X_1 (f_1, f'_1) referred to A, and X_2 (f_2, f'_2) referred to B. Then, since parallel rays on emergence from the system come from F_2, F_2 is the image of F in S_1. Therefore the line joining X_1 and F_2 on the y axis will cut the x axis in F.

Again, since parallel rays on incidence go to F'_1 and thence to F', F' is the image of F'_1 in S_2. Therefore the line joining X_2 and F'_1 on the x axis will give F' on the y axis.

The principal foci of any system of surfaces may be determined in like manner.

9. In the case of a lens the distances AF, BF' may be readily found as follows in terms of $f_1, f_2, \ldots$

From the similar triangles FAF_2, $X_1F'_1F_2$ (fig. 4), we have

$$\frac{AF}{AF_2} = \frac{F'_1 X_1}{F'_1 F_2}; \quad \text{that is } \frac{AF}{f_2 - e} = \frac{f_1}{f'_1 + f_2 - e},$$

where $AB = e$.

Also from the similar triangles $F'BF'_1$, $X_2 F_2 F'_1$,

$$\frac{BF'}{BF'_1} = \frac{F_2 X_2}{F_2 F'_1}; \quad \text{that is, } \frac{BF'}{f'_1 - e} = \frac{f'_2}{f'_1 + f_2 - e}.$$

These values can also be deduced from the relation of § 3. Thus, taking the x axis of the figure, we have

$$F_1 F \cdot F'_1 F_2 = f_1 f'_1, \ \&c.$$

10. In the system referred to in § 6 the images $(\omega_1, \omega_2, \ldots)$ which an object ω_0 at R_0 produces at $R_1, R_2, \ldots$, may be

determined as Helmholtz does (*Optique Physiologique*, p. 74), or as follows:—

Let O_1 be the centre and f_1, f'_1 the principal focal lengths of S_1, &c.

Then (fig. 5)

$$\frac{\omega_1}{\omega_0} = \frac{O_1 R_1}{O_1 R_0} = \frac{F_1 X}{R_0 F_1} = \frac{f_1}{d_0} = \frac{d'_1}{f'_1}.$$

In like manner,

$$\frac{\omega_2}{\omega_1} = \frac{f_2}{d_1} = \frac{d'_2}{f'_2}, \text{ &c.}$$

From these relations we find

$$\frac{\omega_2}{\omega_0} = \frac{f_1 f_2}{d_0 d_1} = \frac{d'_1 d'_2}{f'_1 f'_2},$$

$$\frac{\omega_3}{\omega_0} = \frac{f_1 f_2 f_3}{d_0 d_1 d_2} = \frac{d'_1 d'_2 d'_3}{f'_1 f'_2 f'_3}, \text{ &c.,}$$

Hence if $\omega_0 = \omega_n$, the nth equality becomes $= 1$, and the points R_0, R_n the principal points of the system. Thus, if $n = 2$, $d_0 d_1 = f_1 f_2$, $d'_1 d'_2 = f'_1 f'_2$.

Also, since $AR_1 = f'_1 - d'_1$, $BR_1 = f_2 - d_1$, we have

$$d_1 + d'_1 = f'_1 + f_2 - e;$$

and the values of the principal focal lengths become

$$f = \frac{f_1 f_2}{f'_1 + f_2 - e}, \quad f' = \frac{f'_1 f'_2}{f'_1 + f_2 - e}.$$

11. Now let R, R′ be the principal points, F, F′ the principal foci of a thick lens; so that we have

$$\frac{f}{p} + \frac{f'}{p'} = 1. \quad \ldots \ldots \quad (4)$$

Fig. 6, in which X is the point (f, f'), exhibits the method of finding the conjugate of a given point.

12. Conjugate points will be nodal points N, N′ when on the x axis we have $NN' = RR'$. This will evidently happen when (fig. 6) the line through X makes $FN = FX$. $RN (= f' - f)$ on the x axis will then be equal to $R'N'$ on the y axis.

If distances are measured from the nodal points N, N′, equation (4) becomes $\dfrac{f'}{p} + \dfrac{f}{p'} = 1$, in which f', p are measured from N, and f, p' from N′; and the conjugate points are determined as in fig. 7.

13. These figures make the existence of self-conjugate points manifest. Thus in fig. 7, if S is such a point, we have

$$FS \cdot F'S = ff', \quad FS + F'S = FF' = 2h.$$

Hence FS, F'S are the roots of $s^2 - 2hs + ff' = 0$, and the self-conjugate points are at equal distances from F, F'.

14. Fig. 8 exhibits the construction when one of the self-conjugate points is taken as origin.

From the similar triangles PP'P, S'P'X, and also PSP, FSF, we obtain the relations

$$\frac{PSP'}{S'P} = \frac{PP}{S'X} = \frac{PP}{FF} = \frac{SP}{SF}.$$

15. If F is the image of K, and K' of F', then on the x axis of fig. 8 we have, § 7,

$$FK \cdot FF' = FS \cdot F'S = FF' \cdot F'K'.$$

Hence

$$FK = F'K' = \frac{ff'}{2h}.$$

Also, if T, T' are conjugates such that $FT = F'T'$, then

$$FT^2 = FT \cdot F'T' = ff'.$$

It thus appears that the middle point of FF' also bisects the lines KK', SS', RN', R'N, TT' and (*vide* § 28) VV'.

16. Helmholtz's method (§ 6) may be applied as follows to a system of lenses.

Let there be any number of lenses $L_1, L_2, \ldots$ whose principal foci are $(F_1, F'_1), (F_2, F'_2) \ldots$, and whose principal planes cut the common axis in $(A, A'), (B, B') \ldots$

Let $(R_0, R_1), (R_1, R_2) \ldots$ be pairs of conjugate points such that $R_0 F_1 = \partial_0, R_1 F'_1 = \partial'_1, R_1 F_2 = \partial_1, \ldots$ In like manner let $(P_0, P_1), (P_1, P_2), \ldots$ be any other set of conjugate points such that $R_0 P_0 = p_0, R_1 P_1 = p'_1, \ldots$

Then, § 7,

$$\frac{\partial_0}{p_0} + \frac{\partial'_1}{p'_1} = 1,$$

$$\frac{\partial_1}{p_1} + \frac{\partial'_2}{p'_2} = 1, \&c.;$$

from which, by eliminating $p_1 = -p'_1, p_2 = -p'_2, \ldots$, we get an equation of the form

$$\frac{f}{p_0} + \frac{f'}{p'_n} = 1,$$

where $f = R_0 F, f' = R_n F'$; F, F' being the principal foci of the system.

17. The principal foci F, F′ of a system of lenses may be determined geometrically as in § 8.

Thus, let there be two lenses L_1, L_2, whose principal foci are (F_1, F'_1), (F_2, F'_2), and principal points (R_1, R'_1), (R_2, R'_2). Then (fig. 9), since parallel rays on emergence come from F_2, F_2 is the image of F in L_1. Hence the line joining X_1 and F_2 on the y axis gives F on the x axis. Again, since parallel rays on incidence go to F'_1, and thence to F′, F′ is the image of F'_1 in L_2. Hence the line joining X_2 and F'_1 on the x axis gives F′ on the y axis.

In the construction, of course, any pairs of conjugate points may be employed instead of the principal points.

18. In the system of § 16 the images ω_1, ω_2, ... which an object ω_0 at R_0 produces may be determined as follows:—

Let (f_1, f'_1), (f_2, f'_2), ... be the principal focal lengths of L_1, L_2, ... Then since (§ 20) in a thick lens the ratio of the object to the image is that of their respective distances from the nodal points, we have (fig. 10),

$$\frac{\omega_1}{\omega_0} = \frac{N'_1 R_1}{N_1 R_0} = \frac{F_1 X}{R_0 F_1} = \frac{f_1}{\eth_0} = \frac{\eth'_1}{f'_1}.$$

In like manner we have

$$\omega_2 = \omega_1 \frac{f_2}{\eth_1} = \omega_1 \frac{\eth'_2}{f'_2}$$

$$= \omega_0 \frac{f_1 f_2}{\eth_0 \eth_1} = \omega_0 \frac{\eth'_1 \eth'_2}{f'_1 f'_2}; \text{ \&c.}$$

Hence if $\omega_0 = \omega_n$, R_0, R_n become the principal points of the system, and

$$\eth_0 \eth_1 \cdots = f_1 f_2 \cdots$$
$$\eth'_1 \eth'_2 \cdots = f'_1 f'_2 \cdots$$

19. The equation for the system of lenses being $\dfrac{f}{p} + \dfrac{f'}{p'} = 1$, referred to the principal points, the corresponding equation, when the nodal points are origins, becomes $\dfrac{f'}{p} + \dfrac{f}{p'} = 1$, in which f', p are measured from N, and f, p' from N′.

20. The lengths of object and image at various pairs of conjugate points may now be compared.

Thus (fig. 7), if ω at P gives ω' at P′, we have [*]

$$\frac{\omega + \omega'}{\omega'} = \frac{PR}{PF} = \frac{PF}{RF} + 1.$$

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[*] *Vide* Croullebois, *Lentilles épaisses,* p. 32.

Hence

$$\frac{\omega}{\omega'} = \frac{PF}{FX} = \frac{PN}{P'N'},$$

the relation on which is based the definition of nodal points.

It would seem preferable, however, after having proved the existence of nodal points [*], to reverse these steps, and from $\frac{\omega}{PN} = \frac{\omega'}{P'N'}$ to deduce $\frac{\omega}{\omega'} = \frac{PF}{FX}$, &c.

21. Again, if ω at N gives ω' at N',

$$\frac{\omega f}{RN} = \frac{\omega' f'}{R'N'};$$

$$\therefore \; \frac{\omega}{f'} = \frac{\omega'}{f};$$

that is, the apparent magnitude of ω at F is equal to that of ω' at F'.

22. If ω at S gives ω' at S, then (fig. 7) from the similar triangles SNS, SF'X, XFS we have

$$\frac{\omega}{\omega'} = \frac{NS}{N'S} = \frac{f'}{SF'} = \frac{SF}{f}.$$

In like manner, if ω at S' gives ω'' at S', we have

$$\frac{\omega}{\omega''} = \frac{SF'}{f} = \frac{f'}{SF}.$$

Hence from these two relations we have

$$\frac{\omega}{f'} = \frac{\omega'}{SF'} = \frac{\omega''}{SF}.$$

23. If ω at K gives ω' at F, and ω at F' gives ω'' at K', then (fig. 7)

$$\frac{\omega}{\omega'} = \frac{NK}{N'F} = \frac{F'X}{F'F} = \frac{f'}{2h};$$

and

$$\frac{\omega}{\omega''} = \frac{NF'}{N'K'} = \frac{FF'}{FX} = \frac{2h}{f}.$$

II.

24. The geometrical method of the preceding sections may also be extended to the case of reflection at one or more spherical surfaces. A few examples will suffice to illustrate the method. Thus, for a convex mirror F and F' are coin-

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[*] *Vide* Helmholtz, *Optique physiologique*, p. 75.

cident, f is negative, f' positive; and formula (1) becomes

$$\frac{-f}{p} + \frac{f}{p'} = 1.$$

Hence the line joining conjugate points on the two axes passes through $X(-f, f)$, as in fig. 11.

For a concave mirror the formula is

$$\frac{f}{p} - \frac{f}{p'} = 1,$$

and X is $(f, -f)$, as in fig. 12.

25. In either case we have, from the similar triangles PFX, XF'P' (fig. 11 or 12),

$$\frac{PF}{FX} = \frac{F'X}{P'F'};$$

that is

$$dd' = f^2,$$

which is Newton's formula.

If d and d' be measured from P and P' in accordance with the rule of signs § 1, this formula should be written

$$dd' = -f^2,$$

as also appears by deducing it from the relation $dd' = ff'$ of § 3.

26. The relation between the lengths of the object and image is most readily obtained by making the axes cross at O, the centre of the mirror.

Thus, for a convex mirror we have (fig. 13)

$$\frac{\omega'}{\omega} = \frac{OP'}{OP} = \frac{FX}{PF} = \frac{f}{d}.$$

In the case either of a convex or a concave mirror it may be remarked that, if account be taken of the signs of f, f', d, d', the relation

$$\frac{\omega'}{\omega} = \frac{f}{d} = \frac{d'}{f'}$$

determines whether the image is erect or inverted, the sign of $\frac{\omega'}{\omega}$ being positive in the former case, and negative in the latter.

III.

27. Since writing the above, it has occurred to me that the relation $dd' = ff'$ leads to two other simple geometrical methods for exhibiting the relations between the conjugate points.

Thus, if we separate the two axes FF', FF' so that F in the

x axis coincides with F′ in the y axis, as in fig. 14, then evidently the feet of the ordinates drawn from any point on the hyperbola $xy = ff'$ will be conjugate to one another. This construction gives us a readier means of finding many of the points whose positions have already been discussed.

Thus self-conjugate points are at once given by

$$x(2h - x) = ff';$$

and the points K, K′ (§ 15) by

$$2hx = ff'.$$

Again, H being the middle point of FF′, if H is the image of G, and J of H, we have

$$F'J = \frac{ff'}{h} = 2FK = FG.$$

28. From the construction of the preceding section it appears that the lines joining pairs of conjugate points on the two axes touch the hyperbola

$$4xy = ff'.$$

Fig. 14 shows that the conjugate points V, V′ are equidistant from H, the middle point of FF′, and that

$$FV = F'V' = FT = \sqrt{ff'}.$$

LVI. *On the supposed Repulsion between Magnetic Lines of Force. By* R. H. M. Bosanquet, *St. John's College, Oxford.*

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

THE idea of a repulsion between magnetic lines of force was derived by Faraday from the repulsion which exists between two magnetic needles placed "side by side with like poles in the same direction" (Exp. Res. vol. iii. p. 419).

In the deduction of the forces which accompany lines of force, Maxwell reduces them to a tension along the lines of force combined with a pressure in all directions at right angles to them.

Now it is easy to show experimentally, and indeed it is well known, that rings magnetized by means of a continuous coil uniformly wound round them present no external magnetic action, though they may be the seat of closed circuits of magnetic lines of force of very great intensity. It is clear that in this case we may suppose the ring divided into a number of separate rings, each containing lines of force, and that such

rings will be wholly without action on one another. If, then, such similar rings be placed parallel and close to each other, they do not repel each other, as they should do if there existed a repulsion between parallel lines of force.

Practically, it is impossible to obtain rings so uniformly forged and wound as to be entirely without external magnetic action. This usually manifests itself as a slight polarity, which is easily recognized by a compass-needle, the poles being at the extremities of a diameter. But in my rings this polarity has always been small, even when the induction in the ring was 10,000 or thereabouts. I have suspended two such rings parallel to each other by strings, and made the contacts by the ends of the coils dipping into mercury. But neither by reversing the magnetism of the rings relatively to each other, nor by make and break have I ever been able to cause the smallest movement of the nature of approach or recess of the rings with reference to each other; and this was only to be expected from what is well known.

We may notice that, in the illustration of Faraday, the movement of the system of two parallel needles due to their repulsion leads to a redistribution of the lines of force. It appears therefore that the repulsion here observed must depend upon this redistribution. To illustrate what is meant, suppose the lines of force to exert their tension like elastic bands on a mechanical system such that, when yielding to the tension takes place, the needles are separated. In this case, whenever the lines of force are prevented from changing their form, the repulsion at right angles to them must disappear; and this appears to be what actually happens.

LVII. *On some Thermal and Volume Changes attending Mixture. By* Frederick Guthrie [*].

[The paragraphs are numbered in sequence with those of my previous communications on Salt-Solutions and Attached Water.]

§ 256. IT may be taken as a rule that solid crystalloids are more soluble in liquids when the two are at a higher than when at a lower temperature. The apparent exceptions to this rule are all, I believe, referable to the decomposition by heat which the solids undergo and the inferior solubility of the new products in the liquid.

In §§ 238–241 *a* it was shown that the liquids triethylamine and water are remarkably more miscible when cooler than when warmer; and their relationship in this respect was

pretty fully made out. The conclusion come to in this particular case was that, when the two liquids are brought together, a subcryohydrate is formed, and the heat attending (set free during) its formation may or may not be sufficient to effect its almost complete decomposition, or, rather, mitigate its formation according as the initial temperature of the two liquids is higher or lower. And that subsequent elevation of temperature affects decomposition. Depression of temperature promotes the formation of the subcryohydrate.

A liquid is in a different predicament from a solid when the question turns upon the solubility in a liquid medium. With a solid, increase of temperature always tends in the direction of fusion *per se*, which implies diminished cohesion and the bringing of the two (solid and liquid) into a community of physical state. In the case of two liquids, although, as before, rise of temperature may promote solution by diminishing cohesion, such promotion may be more than counterbalanced by the tendency of the increased heat to separate one or other liquid as a vapour, the particles of which, coalescing, form a liquid insoluble in the rest.

Be this as it may, it will be found that the separation of liquids from their mixtures by increase of temperature is by no means uncommon, and may be the rule rather than the exception long before temperatures approaching the critical ones are reached.

§ 257. *Change of Volume of Triethylamine and Water at about the Temperature of their Separation.*—The remarkable separation which takes place between triethylamine and water when a mixture of the two is warmed, and which was described in § 238, suggests the possible use of such a mixture as a calorimeter. For, if such separation is accompanied by any great change in volume, since the amount of additional heat required to effect a large separation is exceedingly small, a very exact measure of the heat given to the mixture by a given mass of matter cooling through a given range of temperature would be obtained by measuring such change of volume.

I accordingly took a bulb with a capillary stem and determined its capacity up to a lower mark on the stem, and then calibrated the stem. The capacity at $16°\cdot1$ was $9\cdot1823$ cubic centim. The mean volume of 1 millim. of the stem was $\cdot000830038$ cubic centim., or $0\cdot00009039$ of the capacity of the bulb. Into this bulb $5\cdot4873$ grams of water were introduced and then $3\cdot0600$ grams of triethylamine, making a $35\cdot8$-percent. solution. The two on being mixed and brought to the temperature of $16°\cdot1$ had a volume which may be called V,

and which was 9·1820 cubic centim. The bulb was now kept
for an hour at each 0°·5 higher temperature. In the follow-
ing Table the rise in millimetres for every 0°·5 is given ; such
rise being corrected for the calibration of the tube and cor-
rected also for the expansion of the glass (cubic expansion
·000026 for 1° C). The nearest tenths of millimetres only
are given.

TABLE LVIII.

T.	Corrected increase on previous volume.	Corrected increase on original volume.	T.	Corrected increase on previous volume.	Corrected increase on original volume.
	millim.	millim.		millim.	millim.
16·1	...	...	21·6	18·8	172·5
16·6	7·9	7·9	22·1	18·0	190·5
17·1	7·9	15·8	22·6	17·5	207·0
17·6	7·9	23·7	23·1	17·0	224·0
18·1	8·4	32·1	23·6	17·3	241·0
18·6	15·5	47·6	24·1	17·2	258·2
19·1	24·5	72·1	24·6	17·2	275·4
19·6	24·6	96·7	25·1	17·2	292·6
20·1	20·8	117·5	25·6	17·1	309·7
20·6	18·6	136·1	26·1	17·1	325·8
21·1	17·6	153·7	26·6	17·1	343·9

The original volume at 16°·1 being 9·1820 cubic centim.,
at, for example, 19°·1 it was 9·182 + 72·1 × ·00083001 *, or
9·2418 cubic centim. As the volumes in the third column
are corrected for calibre, they serve at once to explain the
behaviour of the liquid.

From § 237 it seems that the liquid here dealt with is, at
starting, at 16°·1 a mixture of the subcryohydrate and the
base itself. This mixture expands regularly from 16°·1 to
17°·6. Through that range equal increments of temperature
are accompanied by equal expansions. At 18°·1 the liquid
is opalescent, and that opalescence is accompanied by an in-
creased expansion. At 18°·6 the liquid becomes quite milky,
and on standing separates into two of nearly the same density
and refractive index. These two are about equal in volume (see
§ 241 a). The two next half-degree warmings produce a still
greater separation ; I mean that the total actual sinking of
the watery solution and the rise of the ammoniacal solution is
probably greater in this case than before. The joint expan-
sion has increased. Now this may be brought about by two
causes : either that the separation is greater, or that after
separation the mean expansion by heat of the separated parts

* From table of calibration.

together is greater. That the increased expansion is not due to the second of these causes seems proved by the fact that, as the heating is continued, the expansion—although, indeed, always greater than that at temperatures below the separating point—is less than the expansion during separation. Separation produces some expansion ; and this being superadded to the expansion due to the increased temperature of the separated constituents gives rise to the elegant curve of fig. 1. The lower and upper parts of this curve are straight lines at different inclinations to the axis. The region of separation is indicated by a curve tangent to both, and whose mean tangent is more inclined than either to the axis of percentage.

Although, therefore, the separation of the mixed liquids into two immiscible liquids (each of which is mixed) is accompanied by an abnormal volume-change (increase), this increase is not so much larger than the increase attributable to mere heat-dilatation as to make the liquid even at the brink of its critical condition especially valuable as a calorimeter.

Fig. 1.

Expansion of Triethylamine and water, before, during, and after separation.

16°·1 17·1 18·1 19·1 20·1 21·1 22·1 23·1 24·1 25·1 26·1
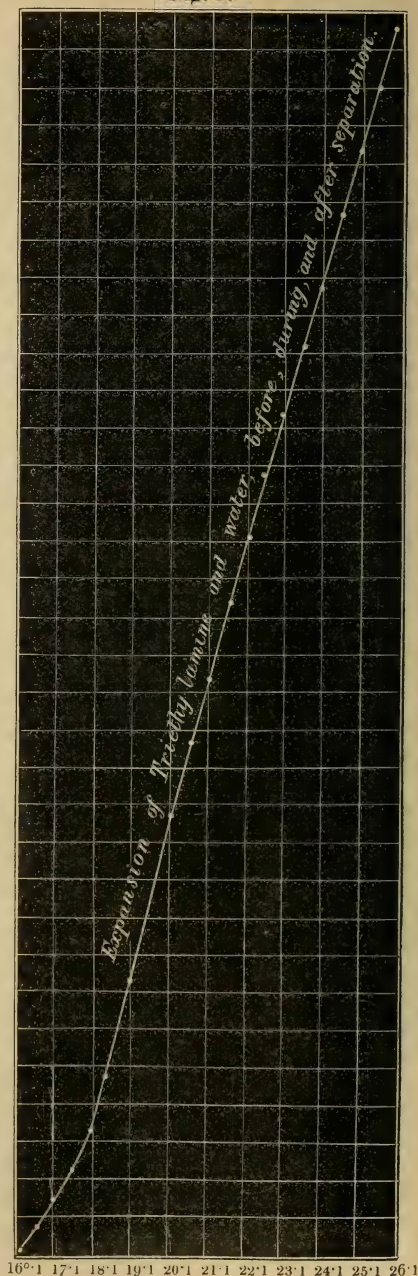
Another resource would be of course to measure the degree of separation approximately by measuring the height of the plane of separation of the two immiscible mixed liquids heated by a known mass cooling through a known range. This would be indeed in theory a very effective calorimeter; but I do not see the way at present to overcome certain practical difficulties of arrangement and manipulation.

§ 258. *Diethylamine and Water.*—These two liquids appear to mix in all proportions at all atmospheric temperatures above 0° C. An aqueous solution of the base, when heated in an open vessel, gives off the base as a vapour, and the temperature does not rise above 100° C.

Into a strong glass tube, which was afterwards sealed, was introduced a mixture consisting of 45·42 per cent. of diethylamine and 54·58 per cent. of water. On heating this in an oil-bath, with a thermometer, very gradually, and again letting the temperature fall slowly, the bath being kept well stirred, the following changes were observed :—

At 130° the liquid was still quite clear.

134°·5 separation was incipient.

135°. The lower layer amounted to about $\frac{1}{5}$ of the whole.

136°.	,,	,,	,,	$\frac{1}{4}$	,,
140°.	,,	,,	,,	$\frac{2}{7}$	,,
145°.	,,	,,	,,	$\frac{1}{3}$	,,
150°.	,,	,,	,,	$\frac{1}{3}$	,,
160°.	,,	,,	,,	$\frac{1}{3}$	,,

The conditions were not such as to allow of exact measurement. The critical temperature is, however, trustworthy ; and the result shows that, within a range of about 10° C. only, the separation begins and is completed, as far as the completion is faithfully measured by the height of the plane of demarcation. It is to be noted that, owing in part to the refractive index of diethylamine being nearer that of water than is the refractive index of triethylamine, the above separation is not marked by the milkiness which characterizes the separation of the latter body *. If it were not for accidental dust-particles floating on the surface of the lower liquid it would be, in some cases, almost impossible to distinguish the two layers. As the phenomenon of separation is one which

* Mr. Illingworth, a student in my physical laboratory, has been kind enough to determine the refractive indices of this group.

$$\rho$$

Ethylamine	....	1·3718
Diethylamine	....	1·3850
Triethylamine	..	1·3999

The determinations were made at 17° C., a temperature rather perilously near the boiling-point of ethylamine.

has to be watched for, the tubes cannot be enclosed in metal cases for the purpose of equalizing the pressure on the glass. Although only one tube of this series has burst, I have not cared to carry the temperature above 180° C., which must correspond to a pressure of about 15 atmospheres.

<div align="center">

TABLE LIX.

Separation between Diethylamine and Water as Liquids.

</div>

Diethylamine per cent.	Water per cent.	Temperature at which separation begins.		
12·64	87·36	Still clear at		180°.
15·02	84·98	Begins to separate at		128°.
16·30	83·70	,,	,,	121·8.
20·94	79·06	,,	,,	121.
26·89	73·11	,,	,,	123.
37·80	62·20	,,	,,	128.
45·42	54·58	,,	,,	134·5.
62·35	37·65	,,	,,	154.
75·76	24·24	Still clear at		170 (burst about 180°).

<div align="center">

Fig. 2.

Diethylamine and Water.

</div>
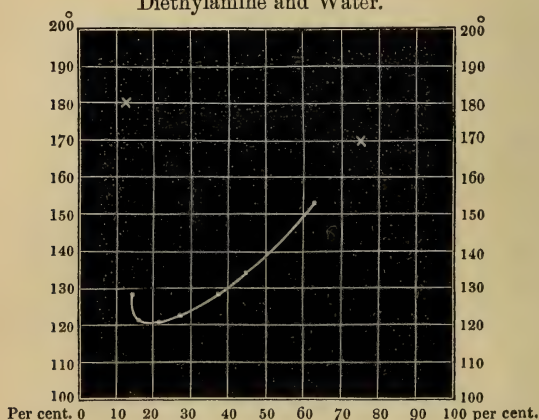
A few points are noticeable in these experiments. The 12·64-per-cent. solution showed no true separation at 180°. On standing to cool, with the point of the tube a little above the oil, a layer was formed on the liquid surface of about 1 millim. in thickness. This layer subsisted even when the temperature of the bath had sunk to 100°, provided the tube was not shaken. On repeating the experiment, and removing the tube from the bath at 180°, it became evident that the phenomenon was one of distillation. The upper and partly empty end of the tube being the first to cool, the liquid of highest vapour-tension, namely the diethylamine, distilled

into that region, condensed, and floated on the heavier and more aqueous portion. Such a layer is rather apt to be overlooked, but its growth may be watched in comfort after the temperature has fairly begun to sink.

§ 259. It should also be remarked that while a 12·64-per-cent. solution at 180° has only a slight etching-action on glass, the 62·35-per-cent. solution caused the surface of the glass (soft German) to peal off in visible scales when heated to 150°–160°, acting like a caustic alkali. This may be the reason of the bursting of the 75·76-per-cent. tube, which had a wall-thickness of 2·5 millim. and an internal diameter of 9 millim. It is well to remember, therefore, that a tube which has withstood a pressure due to a certain temperature may afterwards give way when even at a lower one.

§ 260. I have not succeeded in separating ethylamine from water by heat in closed vessels. But by the closest analogy we must expect both that body and ammonia itself to leave the water with which they are combined as subcryohydrates (§§ 235, 233); and at some very high temperature and pressure to exhibit nearly complete insolubility with that liquid. All of these liquids contract with water and evolve heat.

§ 261. *Tetrethylammonium Oxide.*—Looking on aqueous ammonia as being a solution in water of the oxide $NH_4 HO$, the comparison between ethyl-, diethyl-, and triethyl-ammonium oxides on the one hand, and tetrethyl-ammonium oxide on the other, in regard to their solubilities in water being affected by heat, should present many points of interest both to the physicist and to the chemist. The following experiment may be noted; for although it brings us but little further in the immediate direction of our inquiry, it confirms the statement that a solution of tetrethylammonium is decomposed on concentration by evaporation. A 10-per-cent. solution heated in an oil-bath to 180° gives off a permanent gas which ultimately may burst the tube. This is no doubt olefiant gas. At the same time oily drops which float are formed in the tube; on cooling, they disappear. This is evidently triethylamine containing water; the reaction being

$$(C_2 H_5)_4, NHO = (C_2 H_5)_3, HNHO + C_2 H_4.$$
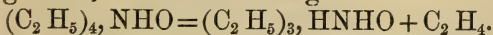
And it appears that this known decomposition is brought about by heat alone without concentration.

§ 262. *Tetramethylammonium Oxide* (a 10-per-cent. solution) does not show any separation at 200°, but begins to solidify at −16°. The tetrethyl compound of the same strength also solidifies in an ice-salt cryogen.

§ 263. *Ethylic Ether* may be here mentioned as a liquid which, though only slightly soluble in water, forms with it a

solution decomposable by heat. Water saturated with ether at a given temperature, and heated in a closed tube a few degrees, becomes visibly milky. When such a solution is heated to 100° C., the ether, probably nearly anhydrous, forms a distinct layer on the top. It is redissolved on cooling. Now in § 104 it was shown that ether united with water. In § 274 it will be shown that such union is accompanied by the liberation of heat and by contraction. Here we have the third term of such relationship, namely, the decomposition of the combination by a rise of temperature.

§ 264. *Alcohol and Bisulphide of Carbon.*—It may be recalled that in §§ 207–228 strong, almost perfect, analogies were established between water-salt alloys and salt-salt alloys. So, now, I am led to consider the case of the mixture of two liquids neither of which is water. And in choosing for my first experiments alcohol and bisulphide of carbon, I was guided by the fact that, speaking from a chemical point of view, we should not expect there to be any relationship, and because both liquids can be got in a state of very great purity. The alcohol was obtained by distilling the nominally "absolute" from quicklime. The bisulphide was washed with water and distilled from oil of vitriol. A preliminary experiment showed that expansion resulted on mixing the two. A quill-tube about 4 feet long was closed at one end and half filled with the bisulphide; about an equal volume of alcohol was added. The tube was closed and the contents mixed. When the whole had resumed the air-temperature, a permanent lengthening of the column of about 11 millim. had taken place.

For exact determination the following method was employed. Two bulbs, A and B, nearly equal, were blown on a piece of thermometer-tubing of rather large bore (about 1 millim. internal diameter), the neck between the bulbs having the same width and being as short as practicable; the bulbs being weighed, bisulphide was introduced through a very fine capillary tube, until the lower bulb was filled at 17°·6. The whole was again weighed. The upper bulb and the lower part of the stem being filled with alcohol, the height f was noted at which the liquid stood at 17°·6. A third weighing followed. On tilting and frequently inverting, the two could

Fig. 3.

be perfectly mixed. When brought again to 17°·6, the height g was observed. The volume of the capillary from f to g is got by measuring the length, and weighing a column of mercury which has a length (exactly measured) of about the length f–g.

> Actual weight of bisulphide . . 1·8180 gram.
> ,,   ,,   alcohol . . . 1·9856 ,,
> Reduced expansion (at 17°·6) . 0·02912 cub. cent.

This gives an expansion of 0·007405 of the original joint volume. The method is seen to be one capable of extreme accuracy, and is, I think, though more laborious, preferable to a specific-gravity method, because the temperature is better under control. This individual result has, however, no special numerical significance, because the two liquids are not in any simple relationship by weight or volume, and because, as we should expect and as we shall see is the case (§ 271), the ratio of change of volume depends upon the ratio of the constituents.

It is important to note that the increase in volume here observed is accompanied by a fall in temperature, which at first, and until the temperature is recovered, tends to reduce the volume. This, the natural corollary of expansion, will be examined later.

§ 265. Alcohol and bisulphide of carbon mix with one another in all proportions at all temperatures between 0° and 100° C. This fact does not seem to be generally known, the reason perhaps being that a very small quantity of water prevents the perfect mixture taking place between some proportions of the nominal constituents. The examination of the simultaneous reciprocal solubilities of the three bodies alcohol, bisulphide, and water would be a fascinating inquiry, but a very onerous one; for many thousand experiments would have to be performed in order to trace the effect of even a few variations in temperature and in the threefold ratio. Moreover, the complication would be much further increased by the chemical attitude between alcohol and water.

§ 266. I made nine mixtures of alcohol and bisulphide containing the two liquids in different ratios. The liquids were weighed in tubes closed at one end, and having capillary necks, which were then sealed off. These solutions, when used, were transferred to open tubes, which were then cooled in an ordinary ice-salt cryogen with the following results.

TABLE LX.

Separation of Alcohol and Bisulphide of Carbon by Cold.

Per cent. of bisulphide.	Per cent. of alcohol.	Temperature at which separation begins.
94·94	5·06	Remains clear down to −18°·4.
89·54	10·46	Becomes turbid at ......−14°·4.
84·89	15·11	,, ,, ...−15°·9.
79·96	20·04	,, ,, ...−16°·1.
65·11	34·89	,, ,, ...−17°·7.
59·58	40·42	
49·91	50·09	Remains clear down to −20°.
39·96	60·04	
29·92	70·08	

In these experiments, as the thermometer sinks it is noticed that at several degrees above that at which separation begins the liquid becomes opalescent, or rather fluorescent; for in this state it is still perfectly transparent, and colours the transmitted light of a light orange-yellow. It is pale blue by the fluoresced light. On reaching the critical temperature of true turbidity, the change is abrupt. At only the fraction of a degree lower the liquid divides into two with surprising suddenness and precision. In the case of the 79·96-per-cent. mixture the volumes of the two separated liquids are about equal at −17°, although at −15° only the above-mentioned fluorescence betrays the impending change. The suddenness of the change argues that the quantity of heat lost during the change is inconsiderable. Again, on removing from the freezing-mixture and shaking up, I have not been able to detect anything like a stationary thermometer during remixture, although all analogy shows that there must be a tendency that way. Indeed the phenomenon closely resembles that described in §§ 238–241a attending the decomposition of an aqueous solution of triethylamine. But it is here presented with a falling thermometer, there with a rising one. Here it resembles the separation of a solid salt containing water of crystallization from an aqueous solution which still retains some : there it was due to the decomposition by heat of a subcryohydrate. Here the original mixing absorbed heat, as when a salt dissolves in water : there it liberated heat. Here such mixing gained volume: there it lost volume. The one case is, as it were, a real image of the other, and inverted, because real.

Only such a little bit of this behaviour is revealed by an ice-salt cryogen that it would be almost useless to draw its curve from these four points. Laid out in percentages of

alcohol from left to right, it seems as though its shape would be like that of the reflexion in the axis of percentages of the curve of diethylamine and water (fig. 2).

Alcohol, Bisulphide of Carbon, Amylene, Ether, Chloroform, and Benzol.

§ 267. Perhaps we may take the relationship between alcohol and bisulphide of carbon as being typical of such a relationship as resembles the solution of nitre in water, or of fused nitre in fused nitrate of sodium (§ 220) (which results in expansion of the solidified alloy), or, lastly, the solubility of fused nitre in water under pressure (§ 252). The method of experimenting adopted reveals, however, somewhat unexpected relationships between other liquids, which relationships are of a more chemical character. Many chemists have of late years made great use of the term " saturation," and the expression has been of some real service. But its unguarded use has, I venture to say, given rise to some misconception. The word itself certainly conveys something absolute and complete; and it is undoubtedly intended to convey such an idea, especially when prefixed by " perfect " or contrasted with " partial." It is only necessary to revert to the types of physical saturation upon which the analogies of chemical saturation are based, to show that such condition is relative and not absolute. Chemical saturation is not a remote analogue of electric neutrality, and the latter is clearly relative.

§ 268. Two or three tubes were made, similar in principle to that of fig. 3, but of more general use (fig. 4). In one of these the lower and upper bulbs (up to a subsequently marked point on the stem) were of absolutely the same capacity (between 3 and 4 cub. cent.). In the second the lower bulb was several times as big as the upper. By adding weighed quantities of mercury to the lower bulb, the ratio of contents could be changed at will.

Fig. 4.

In order to give an idea of the absolute and relative dimensions, I may state that in one of the tubes the exact capacity of *a* and *bf* at 17°·6 was 3·3777 c. c., the total volume upon
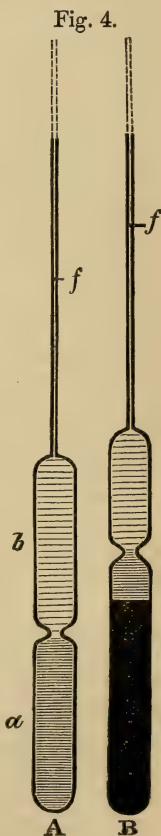
which the expansion or contraction took place being therefore 6·7554 c. c. The mean volume of 1 millim. of the capillary tube about *f* was 0·00140183 c. c.; so that 1 millim. on the capillary meant 0·00020737 of the joint liquid volumes. As the readings could be made by means of a cathetometer* to within 0·2 millim., I imagine that the numerical results are strict to the fifth decimal place. The only other sources of error appear to be the mixing of the liquids during the filling of the upper bulb and capillary. The filling of both bulbs is effected by means of a funnel-capillary, which reaches about half way down into the bulb which has to be filled. Accidental soiling of the tube is removed by a thin German-silver cotton-covered wire.

In the following Table equal volumes at 17°·6 of the liquids enumerated were taken. There is in every case an expansion marked +, or a contraction marked −. Before these signs is H, C, or according as heat is liberated or absorbed. Immediately beneath these signs is the amount of contraction upon one volume of the original liquids taken jointly (before mixture). Below these is the temperature to which the altered volume has to be brought in order to restore it to the original (joint) volume.

Table LXI.
Equal Volumes at 17°·6.

	Alcohol.	Ether.	Bisulphide of Carbon.	Amylene.	Chloroform.	Benzol.
Alcohol	0	H− ·006894 23°·5	C+ ·007278 11°	?	H− ·002488 19°·75	C+ ·0002488 17°·42
Ether	......	0	C+ ·001556 16°·5	H− ·0004977 18°·1	H− ·0108869 25°·8	H− ·00346308 20°·4
Bisulphide of Carbon......	......	......	0	C+ ·00311055 15°·05	C+ ·00688468 11°·7	C+ ·0069469 11°·1
Amylene ...	......	......	.. ...	0	H− ·0015138 19°·1	C+ ·0010783 16°·6
Chloroform .	......	......	......	......	0	C+ ·00183969 15°9
Benzol	......	......	......	......	......	0

The experimental errors appear here to be entirely due to

* Designed and made by the "Cambridge Scientific Instrument Company."

(1) the diffusion during the second filling of the two liquids against gravity, an operation which lasts about 15 minutes, and (2) the imperfect purity of the substances. The first of these is quite negligible, as the common surface is only about 1 square millimetre, while the volumes are over 3 cubic centimetres.

In taking the tube out of its bath it is tilted, bulb upwards, so as to be at an angle of about 45°. Where the differences of refractive index and of density are great, complete mixture seems to be reached in five or six reversals of a few minutes each *. But in none of the cases given above were the reversals less than 20 in number nor of less duration than 10 minutes each, nor was the manipulation stopped before trial showed that constancy of volume had been reached. Each experiment from first to last takes about five hours. The open end of the capillary may be stopped by a short piece of caoutchouc-tubing containing a glass plug.

§ 269. Returning to Table LXI., a cloud of ideas suggest themselves. The results are obtained on equal volumes at an arbitrary temperature 17°·6 both before and after mixture. Wherever there is gain of volume, there is absorption of heat, cold, diminished heat-tension (C). Wherever there is loss of volume, there is liberation of heat, heating, increased heat-tension (H). These thermal effects are only given qualitatively in the Table, and were actually obtained in a second series of experiments made as follows. Equal volumes of the two liquids were run from burettes into two test-tubes of thin glass, one of about twice the capacity of the other. The narrower was put inside the wider, and both put into water at 17°·6. After sufficient standing, a thermometer in the inner liquid marks nearly the same temperature. The tubes are removed from the water and wiped, the inner one broken through at the bottom and used as a stirrer.

Let us consider, now, two of these cases more exactly, in one of which there is heat and contraction, in the other cold and expansion.

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* In making such experiments as these, the question presents itself— If two colourless (or similarly coloured) liquids have the same refractive index, how shall we know whether they are mixed or not? And if, therewith, they have the same density, how does their emulsion differ at all from their mixture? It is, indeed, unlikely that any two liquids have the same refractive indices or the same density at more than one temperature. And that they should have both refractive index and density alike at more than one temperature involves an improbability of a higher order. Apart from this, however, it is likely that the skin of a liquid has a different (higher) density and a higher refractive index than the mass of the same liquid. (F. G., Phil. Mag. November 1883.)

Ether and Chloroform.
Maximum Rise of Temperature.

§ 270. The liquids were weighed instead of being measured; otherwise they were treated as in § 269, with the exception that two experiments were made in each case ; in the second experiment the thermometer-bulb was brought to the temperature shown in the first experiment before being used.

Table LXII.

Showing Rise of Temperature from 17°·6 on mixing Ether and Chloroform in different proportions by weight.

Ether.	Chloroform.		Rise in temperature.
		Per. cent.	
2	1	or 33·33	8·0
1	1	„ 50·00	11·0
1	1·615	„ 61·8	11·7 ($C_4H_{10}O : CHCl_3$)
1	2	„ 66·66	11·5
1	3	„ 75·00	10·9
1	4	„ 80·00	9·6

As we are here merely searching for a maximum, we may neglect certain effects which would be of the utmost importance under other circumstances. Thus the specific heat of none of the liquids is the same, and each rise of temperature given is weighted with the specific heat of the liquid in which

Fig. 5.
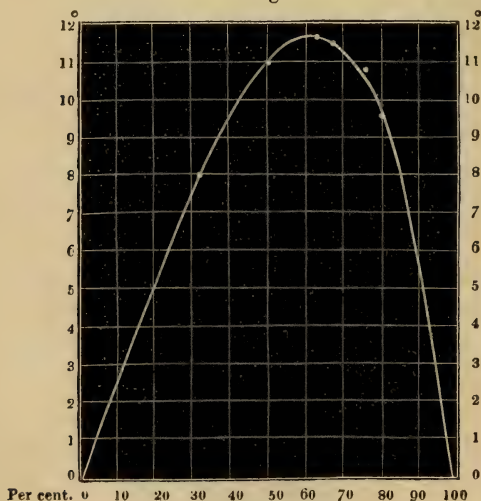
it takes place. But I believe I am right in assuming that this effect would not in this instance materially shift the place of the maximum, although it would alter every one of the individual numbers, and that not in the same proportion.

The curve, fig. 5, shows the relationship of increased heat-tension to the proportions of chloroform and ether by weight by which it is caused.

From these six experiments, therefore, we find that the greatest change (rise) of temperature takes place when the liquids are in the proportion of 1 ether to 1·615 of chloroform by weight, which is the proportion of $C_4H_{10}O$ to $CHCl_3$.

§ 271. This method of experimentation, however, does not allow of such great accuracy as the method of change of volume. If it be found that the greatest change of volume takes place when these weight-ratios (1 ether to 1·615 of chloroform) are mixed, and that a very small change of ratio either way diminishes the change of volume, this evidence will be much strengthened towards the conclusion that the relationship is indeed between molecule and molecule.

Taking, therefore, the tube like A (fig. 3), having equal bulbs of 3·2325 c. c., I put 9·304 grams of mercury into the lower bulb. This reduced the capacity of the lower bulb 0·693 c. c., bringing it to 2·5390, the upper bulb by 3·2325. They are in the ratio of 1·380 to 1·084, which, again, are in the ratio of the molecular volumes (molecular weights divided by specific gravities) of the two liquids. The ratio-value of the capacity of the calibrated capillary-stem has now, of course, to be taken upon a lesser total volume—namely, upon 5·7715 instead of upon 6·4650. The first quantities of chloroform added should be shaken and warmed with the mercury, so as to displace the film of air between the mercury and the glass, or some dissolved gas. If this is not done before the ether is added, air-bubbles arise when the two are mixed, and vitiate the readings.

The result for equimolecular volume at 17°·6 is 0·0116756 : chloroform 1, ether 1·2731.

Instead of 9·304, I now introduced only 9·0 grams of mercury ; this reduced the lower bulb 2·5699 c. c., and the two together to 5·8024; the volume-ratio between the two being 1 chloroform to 1·258 ether. The shrinkage on the new volume was 0·0114783.

Next I introduced 9·6 grams of mercury. This reduced the lower bulb to 2·5241 c. c., and the two together to 5·7566. The volume-ratio between the two is now 1 chloroform to 1·2806 ether. The shrinkage on the new volume was 0·015706.

<div align="center">TABLE LXIII.</div>

VOLUMES.		On being mixed and brought to the same temperature (17°·6) which they had before mixture, shrink to the below-given fraction of the joint volume they had before mixture.
Chloroform.	Ether.	
Per cent.	Per cent.	
50·00	50·00	·0108869
44·29	55·71	·0114783
43·99	56·01	·0116756 ($C_4H_{10}O$, $CHCl_3$)
43·83	56·17	·0115706

The Table shows the great accuracy of which this method is capable, and discovers a maximum contraction exceedingly close to, if not at, the monomolecular ratio; thus confirming the result got by the cruder method of increased heat-tension, § 270.

The liquid solidifies to a white crystalline mass at a constant temperature below 0°, which I shall give when I have determined it exactly.

It seems, then, that ether and chloroform unite chemically with one another to form the body $C_4H_{10}O$, $CHCl_3$, a substance which may be analogous in its composition with S_2Cl_4 $2(C_4H_{10}O)$.

Vapour-tension of Chloroform and Ether Mixtures.

§ 272. The result of the experiments given above will make it imperative to revise previous ideas about the vapour-tension of mixed liquids. The following experiments with ether and chloroform show how the vapour-tension varies with the composition. The absolutely pure and dry substances were mixed in various proportions by weight, and each mixture was introduced into one of a series of perfect barometers in a room of uniform temperature. The barometers stood in the same trough close together. The readings were made with a cathetometer at a distance of nine feet. The readings were made backwards and forwards through the series three times. The atmospheric pressure was made constant by adjusting the mercury in the trough. About five grams of the liquid were introduced into each tube, and in all cases enough, as shown by a rough measurement and calculation, to ensure there being far more than sufficient of each kind of liquid to supersaturate. After determining the mercurial depression, the liquid columns above the mercury were measured, and their specific gravities assumed to be those due to mixture without change of volume. This is not quite true (see § 268). Further, it is assumed that the liquid has the same composition before as after its introduc-

tion into the tube. This, also, is not quite exact. Neither of these errors has been taken into account in the following Table; for they are both of them negligible in comparison with the numerical data sought.

TABLE LXIV.
Vapour-tensions of Mixtures of Chloroform and Ether.
$$T = 19°·02.$$

Chloroform, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression.	Liquid above mercury.	Vapour-tension in millim of mercury at 19°·02.
100	0	200·0	84·0	190·7
90	10	205·2	87·2	196·0
80	20	222·3	106·5	211·7
70	30	236·2	104·0	226·4
63	37	240·2	79·2	233·1
$(C_4H_{10}O, CHCl_3)$ 61·76	38·24	243·9	85·0	236·4
60	40	248·5	81·2	241·4
50	50	285·0	83·3	278·2
40	60	318·7	85·2	312·2
30	70	349·8	77·5	344·8
20	80	383·2	81·8	377·9
10	90	413·8	83·9	408·8
0	100	442·6	90·0	437·8

§ 273. The increase of vapour-tension as the proportion of ether increases is therefore continuous, but by no means regular. There is in the neighbourhood of the monomolecular ratio a diminution in the rate of increase; but immediately this region is past, the curve becomes rectilinear. As the barometer-tubes stand side by side in a row, they present a very interesting appearance, as the mercurial levels form a curve closely similar to that in fig. 6, A (p. 515) turned upside down. Guided by heat-development and shrinkage, we have therefore detected the existence of $C_4H_{10}O, CHCl_3$, and showed that the vapour-tension confirmed the existence of this body. Are we, then, to assume that in every case in Table LXI. where there is heat-development and shrinkage, there is also true chemical union? Reluctant as some may be to admit to the title of chemical compounds a class of bodies which probably numbers many thousands, there seems no help for it. There can be but little doubt, for instance, that ether unites with alcohol and benzol, that chloroform unites with alcohol and with amylene, and so on. The experiments necessary for the proof of this assertion will be laborious, and will require such care and concentration that I must again invite other workers into this fertile field. There is, however, one point which may be here noted. Two elements may unite to complete saturation in respect of one another, yet the molecules so formed may

be quite prepared to unite as a whole with another atom or molecule (compare § 267).

§ 274. The contraction and heating attending the mixing of alcohol and water have been long known. When, in § 98, I described the solid combination of the two, $C_2H_6O, 4H_2O$, and called it a cryohydrate (I should now call it a subcryohydrate), I did not suppose that it was only one of so numerous a family as appears to be the case. In § 104 was briefly described a combination of ether with water. I may here mention the circumstance that equal volumes of the two, when shaken together at 17°·1, rise in temperature to 18°·9. Equal volumes brought together at 17°·6 in the experimental tube of § 268, and agitated by a globule of mercury being made to pass to and fro through the capillary opening, contract 0·005436 of their joint volume, and require to be heated to regain that volume. This contraction is probably very far from the maximum, as there is no doubt a large quantity of passive matter present. For the same reason, the maximum liberation of heat will probably be found with a less water-ratio. Where the maximum heat-liberation occurs we should look for the subcryohydrate, and there also for the maximum contraction.

Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.

§ 275. Taking next an instance where expansion and cold result from mixture, I give at once the numerical results as to the vapour-tensions of the various mixtures.

Table LXV.
Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.
$T = 18°·88$ C.

Bisulphide of Carbon, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 19°·02.
100	0	291·9	78·1	284·5
90	10	353·3	77·5	346·3
80	20	380·8	75·0	374·3
70	30	404·1	82·8	387·3
60	40	416·5	81·2	410·1
50	50	425·2	80·0	419·3
40	60	441·0	90·9	424·6
30	70	434·8	75·0	429·8
20	80	438·1	83·4	433·0
10	90	437·2	81·7	432·5
0	100	436·5	81·7	432·1

Specific gravity of ether, 0·72 ; of bisulphide of carbon, 1·23.

§ 276. Laid out graphically we get accordingly the curve B, fig. 6. Perhaps the most notable character of this curve is its descent at the upper right end. This means that, although bisulphide of carbon has a lower vapour-tension than ether, a little bisulphide loosens the ether and raises the vapour-tension. The effect on the vapour-tension of the liquid brought about by the addition of a little ether to the bisulphide is much more marked.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.

§ 277. Referring again to Table LXI. it is seen that, with whatever of the liquids there examined bisulphide of carbon is mixed, expansion occurs and the temperature is lowered. With chloroform these results are very marked; and having examined the relationship between bisulphide and ether and between chloroform and ether, let me describe the relationship between chloroform and bisulphide of carbon.

TABLE LXVI. *a.*

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.

$T = 16°·0$ C.

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 16°.
0	100	269·9	53·1	264·8
3	97	271·8	58·2	266·2
5	95	277·5	74·9	270·4
10	90	271·6	57·8	266·1
15	85	272·3	56·2	266·8
20	80	273·0	61·9	266·9
30	70	270·7	70·7	263·7
40	60	265·8	60·2	259·7
50	50	260·3	61·3	254·0
60	40	249·6	56·0	243·7
70	30	241·0	60·0	234·6
80	20	227·9	60·5	221·4
90	10	215·4	80·8	206·6
100	0	176·2	64·6	169·2

Spec. grav. of bisulphide of carbon, 1·23; of chloroform, 1·49.

§ 278. On laying these numbers out graphically, the curve C, fig. 6, presents itself. Although we are dealing here with millimetres, the shape of the curve towards pure bisulphide of carbon required confirmation. I therefore employed a

temperature of nearly 2° C. lower ; and having prepared fresh examples of the liquids with equal care, and having changed the barometer-tubes, I found :—

TABLE LXVI. *b.*

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.

$$T = 13°\cdot8 \ C.$$

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 13°·8.
0	100	·259·5	83·0	251·6
5	95	266·0	108·1	255·7
10	90	260·3	91·0	251·5
15	85	258·5	85·2	250·3
20	80	255·5	70·9	248·6
30	70	252·5	70·9	245·4
40	60	248·0	73·3	240·6
50	50	243·5	83·0	235·0
60	40	236·1	78·2	227·8
70	30	220·3	59·5	214·0
80	20	210·7	76·5	202·3
90	10	199·1	78·1	190·4
100	0	170·0	113·2	158·4

Spec. grav. of bisulphide of carbon, 1·23 ; of chloroform, 1·49.

The result seems, then, to be this : The vapour-tension of bisulphide of carbon at 16°·0 is 264·8 millim., at 13°·8 it is 251·6 millim., both referred to mercury at those temperatures. Of chloroform the vapour-tensions at these two temperatures, also referred to mercury at the same temperature, are 169·2 and 158·4. A very great increase of the vapour-tension is brought about by mixing a very little bisulphide with the chloroform ; a little rise is brought about by mixing a little chloroform with the bisulphide. The graphic interpretations of the two Tables LXVI. *a* and LXVI. *b* are shown in curves C and D, fig. 6.

§ 279. If we could find two liquids showing neither contraction nor expansion when mixed, and neither liberating nor absorbing heat, the vapour-tension of a mixture of such liquids should be expressed by the equation

$$vt_{(ma+nb)} = vt_a + \frac{ma(vt_b - vt_a)}{ma + nb},$$

where generally vt_s means the vapour-tension of the liquid s, and where a and b are the liquids and m and n their respective

Fig. 6.
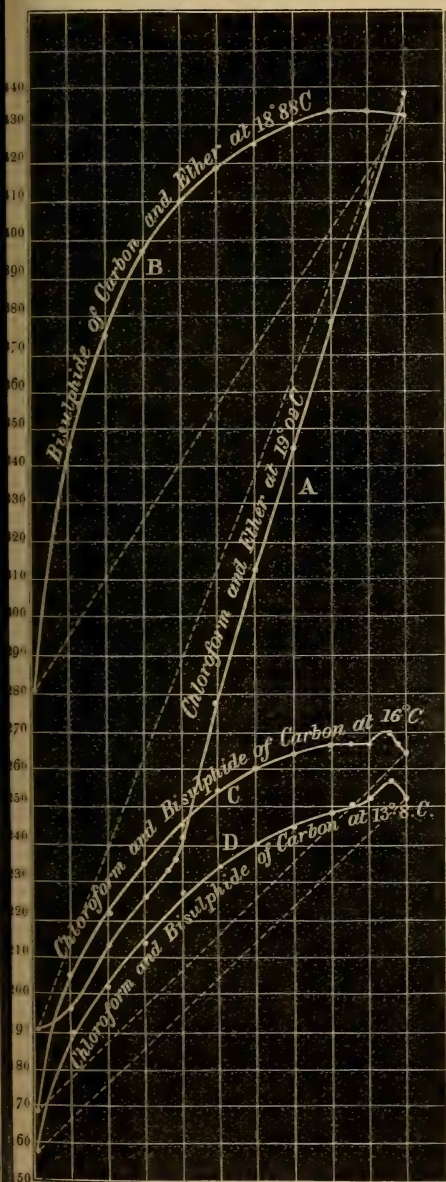
Fig. 7.
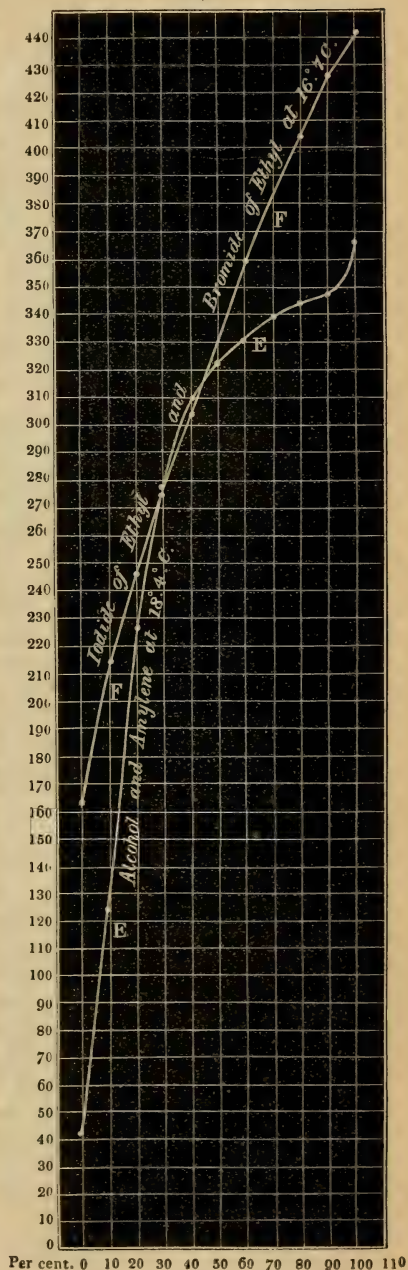
masses. The vapour-tension curve would be a straight line joining the vapour-tensions of the constituents. The maximum departure from this straight line on the curves in fig. 6 gives us the maximum interference. This, in the case of chloroform and ether, is at the monomolecular ratio. Now, if we search the curve of mixtures containing bisulphide of carbon, we find there also a maximum departure from the mean at a certain ratio. In the case of bisulphide of carbon and ether this is at 30 or 35 per cent. of the ether (say 32·5). This implies that the maximum departure from the mean takes place where 1 molecule of ether ($C_4H_{10}O$) is mixed with 2·02 molecules (say 2 molecules) of CS_2. At this ratio we may suppose there to be no indifferent or inert matter. If we consider chemical union to be due to an action of attraction, and regard the maximum thermal or volume effects as taking place when there is no superfluity of either constituent, so here we have an equally distinct molecular ratio, and an absolutely definite one (at all events at a given temperature), where a sort of anti-union takes place—a maximum effect of repulsion. This is a state of things for which some new nomenclature may be necessary. There may be as many anticombinations as there are combinations ; and the former may be quite as definite in weight-ratio as the latter. The essential difference is that, while attraction may result in the production of new stuffs, the latter has the locally opposite action.

Again, with chloroform and bisulphide the maximum departure from the mean is at 40 per cent. bisulphide. This signifies 1 molecule chloroform to 1·05 molecule bisulphide. I therefore submit these formulæ—

$$C_4H_{10}O \longleftrightarrow 2CS_2,$$
$$CHCl_3 \longleftrightarrow CS_2.$$
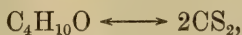
What is the relative nature of the bodies which should give a straight line on the vapour-tension curve of their various mixtures? Such may probably be found amongst hydrocarbons. I find that when equal volumes of ethylic and amylic alcohols are mixed at 13°·9, the temperature rises to 15°·1, implying the formation of a species of double alcohol. Referring to Table LXI. (§ 268) and to the few representative bodies there considered, we find that amylene and alcohol are almost without volume-change.

An examination of the vapour-tensions of their mixtures gave the following numbers :—

TABLE LXVII.

Alcohol, per cent.	Amylene, per cent.	Mercury.	L. C.	Sp. gr.	Cor-rection.	V.-T.
100	0	46·2	73	·79	4·3	41·9
90	10	129·8	99	·78	5·7	124·1
80	20	232·2	85	·76	4·8	227·4
70	30	282·1	85	·75	4·8	277·3
60	40	313·9	90	·73	4·9	309·0
50	50	329·0	98	·72	5·3	323·7
40	60	335·3	101	·71	5·3	330·0
30	70	339·6	100	·69	5·1	334·5
20	80	340·7	117	·68	5·9	334·8
10	90	344·1	121	·67	6·0	338·1
0	100	362·0	112	·66	5·5	356·5

T = 18°·4 C.   Spec. grav. of alcohol, ·79 ; of amylene, ·66.

The curve is seen in fig. 7, E (p. 515).

Through the favour of my colleague, Dr. Hodgkinson, I obtained some pure iodide and bromide of ethyl. These were again washed, dried, and redistilled. The following Table shows the vapour-tensions of their mixtures. They were shielded from the light when in contact with the mercury.

TABLE LXVIII.

Iodide of ethyl.	Bromide of ethyl.	Mercury.	L. C.	Sp. gr.	Cor-rection.	V.-T.
0	100	459	65	1·40	6·8	452·2
10	90	439	100	1·45	10·8	428·2
20	80	415	88	1·50	9·8	405·2
30	70	389	74	1·55	8·6	380·4
40	60	372	93	1·60	11·1	360·9
50	50	343	87	1·65	10·7	332·3
60	40	316	76	1·70	9·6	306·4
70	30	286	73	1·75	9·6	276·4
80	20	260	98	1·80	13·1	246·9
90	10	227	88	1·85	12·2	214·8
100	0	172	62	1·90	8·8	163·2

T = 16°·7 C.   Spec. grav. of bromide, 1·4 ; of iodide, 1·9.

The curve F, fig. 7, shows that the vapour-tensions of the mixtures of these two substances lie nearly in a straight line, and that the two substances therefore very closely fulfil the condition of absolute non-interference.

LVIII. *Applications of Möbius's Theorem on the Reversion of certain Series.* By J. W. L. GLAISHER, *M.A., F.R.S.*[*]

Definitions &c., §§ 1, 2.

§ 1. THROUGHOUT this paper the letters $a, b, c, \ldots$ are used to denote prime numbers only.

I. The operator E_n is defined by the equation

$$E_n f(x) = f(x^n),$$

viz. the effect of operating with E_n upon any function of x is to convert it into the same function of x^n. This definition is supposed to hold good for all values of n, positive or negative, integral or fractional.

Since

$$E_m f(x^n) = f(x^{nm}) = E_{nm} f(x),$$

we see that

$$E_n \times E_m = E_{nm} = E_m \times E_n$$

universally, so that, if $n = a^\alpha b^\beta c^\gamma \ldots$, then

$$E_n = E_a^\alpha \times E_b^\beta \times E_c^\gamma \ldots$$

II. The quantities $e_a, e_b, e_c, \ldots$ (in which the suffixes are primes) are supposed to be absolutely independent constants; and by e_{ab} we denote $e_a \times e_b$, by e_{a^2} we denote $e_a \times e_a = e_{a^2}$, and in general, if $n = a^\alpha b^\beta c^\gamma \ldots$, then e_n is defined to denote $e_a^\alpha \times e_b^\beta \times e_c^\gamma \ldots$

It is perhaps most convenient to regard, as in this definition, $e_a, e_b, e_c, \ldots$ as arbitrary quantities merely distinguished from each other by the suffixes $a, b, c, \ldots$; but if we regard them as functions of $a, b, c, \ldots$ respectively, it is to be noticed that they are independent and arbitrary functions of $a, b, c, \ldots$; viz. we have

$$e_a = \phi(a), \ e_b = \psi(b), \ e_c = \chi(c), \ \&c.$$

§ 2. In order that we may have $e_n = \phi(n)$ for all values of n, the function ϕ must be such that $\phi(mn) = \phi(m)\phi(n)$, whence $\phi(n) = n^r$.

Unless, therefore,

$$e_a = a^r, \ e_b = b^r, \ e_c = c^r, \ \ldots$$

(where r may have any value whatever), e_n cannot be the same function of n for all values of n.

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[*] Communicated by the Author.

Möbius's *Theorem,* § 3.

§ 3. Let

$$\mathrm{F}(x) = \frac{1}{(1 - e_a \mathrm{E}_a)(1 - e_b \mathrm{E}_b)(1 - e_c \mathrm{E}_c) \ldots} f(x);$$

then, expanding the factors, we have

$$
\begin{aligned}
\mathrm{F}(x) &= (1 + e_a \mathrm{E}_a + e_{a2} \mathrm{E}_{a2} + e_{a3} \mathrm{E}_{a3} + \ldots) \\
&\quad \times (1 + e_b \mathrm{E}_b + e_{b2} \mathrm{E}_{b2} + e_{b3} \mathrm{E}_{b3} + \ldots) \\
&\quad \times (1 + e_c \mathrm{E}_c + e_{c2} \mathrm{E}_{c2} + e_{c3} \mathrm{E}_{c3} + \ldots) \\
&\quad \times \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad f(x) \\
&= f(x) + \Sigma e_a f(x^a) + \Sigma e_{a2} f(x^{a^2}) + \Sigma e_{ab} f(x^{ab}) \\
&\quad + \Sigma e_{a3} f(x^{a^3}) + \Sigma e_{a2b} f(x^{a^2 b}) + \Sigma e_{abc} f(x^{abc}) \\
&\quad + \quad . \quad . \quad . \quad . \\
&= \Sigma e_n f(x^n),
\end{aligned}
$$

where n has all values of the form $a^\alpha b^\beta c^\gamma \ldots$. The value of e_1 is supposed to be unity.

Now from the given equation we have

$$
\begin{aligned}
f(x) &= (1 - e_a \mathrm{E}_a)(1 - e_b \mathrm{E}_b)(1 - e_c \mathrm{E}_c) \ldots \mathrm{F}(x) \\
&= \mathrm{F}(x) - \Sigma e_a \mathrm{F}(x^a) + \Sigma e_{ab} \mathrm{F}(x^{ab}) - \Sigma e_{abc} \mathrm{F}(x^{abc}) + \ldots \\
&= \Sigma \pm e_n \mathrm{F}(x^n),
\end{aligned}
$$

where n has all values of the forms a, ab, abc, . . . and the sign is positive or negative according as the number of factors is even or uneven.

We thus obtain the theorem:

If a, b, c, . . . be any prime numbers, and if

$$\mathrm{F}(x) = \Sigma e_n f(x^n),$$

where the values of n are all the numbers of the form $a^\alpha b^\beta c^\gamma$ . ., that is, all the numbers which have all their prime factors included among a, b, c, . . ., then

$$f(x) = \Sigma (-1)^r e_n \mathrm{F}(x^n),$$

where the values of n are all the numbers of the forms a, ab, abc, . . ., that is, all the numbers which have all their prime factors included among a, b, c, . . . and which are divisible by no squared factor, and r denotes the number of the prime factors of n.

This is the most general form of the theorem published by Möbius in Crelle's *Journal*, vol. ix. pp. 105–123 *.   The

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* " Ueber eine besondere Art von Umkehrung der Reihen."

mode of proof is different, as Möbius obtained his results by equating coefficients, and without the use of symbolic methods. In his paper Möbius first proves several particular cases of the theorem, but his results are practically of the same generality as the theorem given above.

If the number of primes a, b, c, ... be finite, the number of values to be assigned to n is infinite in the first equation, but finite in the second equation. If the number of primes a, b, c, ... be infinite both series extend to infinity.

Particular Cases of the Theorem, § 4.

§ 4. The most important cases of the theorem are (i.) when a, b, c, ... denote the complete system of prime numbers, and (ii.) when they denote the complete system of uneven prime numbers.

(i.) Putting
$$a = 2, \quad b = 3, \quad c = 5, \ldots$$
and
$$e_2 = 2^r, \quad e_3 = 3^r, \quad e_5 = 5^r, \ldots$$

so that $e_n = n^r$ (§ 2), we obtain the result:—

If
$$F(x) = f(x) + 2^r f(x^2) + 3^r f(x^3) + 4^r f(x^4) + 5^r f(x^5) + \&c.,$$
then
$$f(x) = F(x) - 2^r F(x^2) - 3^r F(x^3) - 5^r F(x^5) + 6^r F(x^6)$$
$$- 7^r F(x^7) + 10^r F(x^{10}) - 11^r F(x^{11}) + \&c.$$

In the first series all the natural numbers occur; in the second only those numbers which are divisible by no squared factor.

(ii.) Putting
$$a = 3, \quad b = 5, \quad c = 7, \ldots$$

and $e_n = n^r$ as before, we find:—

If
$$F(x) = f(x) + 3^r f(x^3) + 5^r f(x^5) + 7^r f(x^7) + 9^r f(x^9) + \&c.,$$
then
$$f(x) = F(x) - 3^r F(x^3) - 5^r F(x^5) - 7^r F(x^7) - 11^r F(x^{11})$$
$$- 13^r F(x^{13}) + 15^r F(x^{15}) - 17^r F(x^{17}) - \&c. ;$$

the first series involving all the uneven numbers, and the second the uneven numbers which contain no squared factor.

In these theorems the value of r is unrestricted.

Putting r equal to zero, we see that, if
$$F(x) = f(x) + f(x^2) + f(x^3) + f(x^4) + f(x^5) + \&c.,$$

then

$$f(x) = F(x) - F(x^2) - F(x^3) - F(x^5) + F(x^6) - \&c. \ ;$$

and if

$$F(x) = f(x) + f(x^3) + f(x^5) + f(x^7) + f(x^9) + \&c.,$$

then

$$f(x) = F(x) - F(x^3) - F(x^5) - F(x^7) - F(x^{11}) - \&c.$$

All the results given in this section are due to Möbius, and in some respects they might be more properly called by his name than the general theorem in § 3.

Two-fold application of the Theorem, § 5.

§ 5. It follows from § 3 that, if

$$F(x) = f(x) + e_2 f(x^2) + e_3 f(x^3) + e_4 f(x^4) + e_5 f(x^5) + \&c.,$$

then

$$f(x) = F(x) - e_2 F(x^2) - e_3 F(x^3) - e_5 F(x^5) + e_6 F(x^6) - \&c.$$

Now suppose

$$f(x) = x + \eta_2 x^2 + \eta_3 x^3 + \eta_4 x^4 + \&c.,$$

where η_2, η_3, η_4, ... are quantities of the same nature as e_2, e_3, e_4, ..., viz. η_2, η_3, η_5, ... are independent, and $\eta_{mn} = \eta_m \times \eta_n$ for all values of m and n.

We thus have

$$\begin{aligned} F(x) = \ & x + \eta_2 x^2 + \eta_3 x^3 + \eta_4 x^4 + \&c. \\ & + e_2(x^2 + \eta_2 x^4 + \eta_3 x^6 + \eta_4 x^8 + \&c.) \\ & + e_3(x^3 + \eta_2 x^6 + \eta_3 x^9 + \eta_4 x^{12} + \&c.) \\ & \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ = \ & \phi(x) + \eta_2 \phi(x^2) + \eta_3 \phi(x^3) + \eta_4 \phi(x^4) + \&c., \end{aligned}$$

where

$$\phi(x) = x + e_2 x^2 + e_3 x^3 + e_4 x^4 + \&c. \ ;$$

and, applying Möbius's theorem, we find

$$\phi(x) = F(x) - \eta_2 F(x^2) - \eta_3 F(x^3) - \eta_5 F(x^5) + \eta_6 F(x^6) - \dots$$

Whenever, therefore, $f(x)$ is of the form $x + \eta_2 x^2 + \eta_3 x^3 + \&c.$, we obtain a formula in terms of the F's not only for $f(x)$, but also for another quantity $\phi(x)$: in fact, since

$$F(x) = f(x) + e_2 f(x^2) + e_3 f(x^3) + e_4 f(x^4) + \&c.,$$

and

$$= \phi(x) + \eta_2 \phi(x^2) + \eta_3 \phi(x^3) + \eta_4 \phi(x^4) + \&c.,$$

we have

$$f(x) = F(x) - e_2 F(x^2) - e_3 F(x^3) - e_5 F(x^5) + \&c.,$$

and

$$\phi(x) = F(x) - \eta_2 F(x^2) - \eta_3 F(x^3) - \eta_5 F(x^5) + \&c.$$

Results deduced from the Theorem, §§ 6–11.
Formulæ involving $\sigma(n)$, §§ 6, 7.

§ 6. Let

$$e_n = n^r \text{ and } f(x) = \frac{x}{1-x}.$$

We then have

$$F(x) = \frac{x}{1-x} + \frac{2^r x^2}{1-x^2} + \frac{3^r x^3}{1-x^3} + \frac{4\,x^4}{1-x^4} + \&c.$$

$$= x + \sigma_r(2)x^2 + \sigma_r(3)x^3 + \sigma_r(4)x^4 + \&c.,$$

where $\sigma_r(n)$ denotes the sum of the rth powers of the divisors of n.

Thus

$$f(x) = x + \quad x^2 \quad + \quad x^3 \quad + \quad x^4 \quad + \&c.$$
$$\phi(x) = x + \quad 2^r x^2 \quad + \quad 3^r x^3 \quad + \quad 4^r x^4 \quad + \&c.$$
$$F(x) = x + \sigma_r(2)x^2 + \sigma_r(3)x^3 + \sigma_r(4)x^4 + \&c.$$
$$e_n = n^r, \qquad \eta_n = 1 ;$$

and by substituting these values in the formulæ of the preceding section, we find

$$x + \quad x^2 \quad + \quad x^3 \quad + \quad x^4 \quad + \&c.$$
$$= \quad x + \sigma_r(2)x^2 + \sigma_r(3)x^3 + \sigma_r(4)x^4 + \&c.$$
$$-2^r \left\{ x^2 + \sigma_r(2)x^4 + \sigma_r(3)x^6 + \sigma_r(4)x^8 + \&c. \right\}$$
$$-3_r \left\{ x^3 + \sigma_r(2)x^6 + \sigma_r(3)x^9 + \sigma_r(4)x^{12} + \&c. \right\}$$
$$-5^r \left\{ x^5 + \sigma_r(2)x^{10} + \sigma_r(3)x^{15} + \sigma_r(4)x^{20} + \&c. \right\}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

and

$$x + \quad 2^r x^2 \quad + \quad 3^r x^3 \quad + \quad 4^r x^4 \quad + \&c.,$$
$$= x + \sigma_r(2)x^2 + \sigma_r(3)x^3 + \sigma_r(4)x^4 + \&c.,$$
$$- \left\{ x^2 + \sigma_r(2)x^4 + \sigma_r(3)x^6 + \sigma_r(4)x^8 + \&c. \right\}$$
$$- \left\{ x^3 + \sigma_r(2)x^6 + \sigma_r(3)x^9 + \sigma_r(4)x^{12} + \&c. \right\}$$
$$- \left\{ x^5 + \sigma_r(2)x^{10} + \sigma_r(3)x^{15} + \sigma_r(4)x^{20} + \&c. \right\}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

Equating the coefficients of x^n in these two equations, we obtain the formulæ

$$\sigma_r(n) - \Sigma a^r \sigma_r\left(\frac{n}{a}\right) + \Sigma a^r b^r \sigma_r\left(\frac{n}{ab}\right) - \Sigma a^r b^r c^r \sigma_r\left(\frac{n}{abc}\right) + \ldots = 1,$$

$$\sigma_r(n) - \Sigma \sigma_r\left(\frac{n}{a}\right) + \Sigma \sigma_r\left(\frac{n}{ab}\right) - \Sigma \sigma_r\left(\frac{n}{abc}\right) + \ldots = n^r ;$$

where n denotes any number, and $a, b, c, \ldots$ are its prime factors.

§ 7. These formulæ hold good for all values of r, including $r=0$ and r negative. When $r=1$, $\sigma_r(n)$ becomes $\sigma(n)$, the sum of the divisors of n, and the formulæ become

$$\sigma(n) - \Sigma a\sigma\left(\frac{n}{a}\right) + \Sigma ab\sigma\left(\frac{n}{ab}\right) - \Sigma abc\sigma\left(\frac{n}{abc}\right) + \ldots = 1,$$

$$\sigma(n) - \Sigma\sigma\left(\frac{n}{a}\right) + \Sigma\sigma\left(\frac{n}{ab}\right) - \Sigma\sigma\left(\frac{n}{abc}\right) + \ldots = n.$$

When $r=0$, $\sigma_r(n)$ becomes $\nu(n)$, the number of the divisors of n, and the two formulæ coalesce, each reducing to

$$\nu(n) - \Sigma\nu\left(\frac{n}{a}\right) + \Sigma\nu\left(\frac{n}{ab}\right) - \Sigma\nu\left(\frac{n}{abc}\right) + \ldots = 1.$$

Formulæ involving $\Delta_r(n)$, § 8.

§ 8. Let $e_2 = 0$ and $e_p = p^r$, p being any uneven prime, and, as in the last section, let

$$f(x) = \frac{x}{1-x}.$$

Then

$$\mathrm{F}(x) = \frac{x}{1-x} + \frac{3^r x^3}{1-x^3} + \frac{5^r x^5}{1-x^5} + \frac{7^r x^7}{1-x^7} + \&c.,$$

$$= x + \Delta_r(2)x^2 + \Delta_r(3)x^3 + \Delta_r(4)x^4 + \&c.,$$

where $\Delta_r(n)$ denotes the sum of the rth powers of the uneven divisors of n.

Thus we have

$$f(x) = x + \quad x^2 \quad + \quad x^3 \quad + \quad x^4 \quad + \&c.,$$
$$\phi(x) = x + \quad 3^r x^3 \quad + \quad 5^r x^5 \quad + \quad 7^r x^7 \quad + \&c.,$$
$$\mathrm{F}(x) = x + \Delta_r(2)x^2 + \Delta_r(3)x^3 + \Delta_r(4)x^4 + \&c.,$$
$$e_{2n} = 0, \quad e_{2n+1} = (2n+1)^r, \quad \eta_n = 1;$$

and by substituting these values in the formulæ of § 5, and equating coefficients as in the last section, we obtain the formulæ :—

$$\Delta_r(n) - \Sigma\mathrm{A}^r\Delta_r\left(\frac{n}{\mathrm{A}}\right) + \Sigma\mathrm{A}^r\mathrm{B}^r\Delta_r\left(\frac{n}{\mathrm{AB}}\right) - \ldots = 1,$$

$$\Delta_r(n) - \Sigma\Delta_r\left(\frac{n}{a}\right) + \Sigma\Delta_r\left(\frac{n}{ab}\right) - \Sigma\Delta_r\left(\frac{n}{abc}\right) + \ldots$$

$$= 0 \text{ or } n^r, \text{ according as } n \text{ is even or uneven };$$

where $\mathrm{A}, \mathrm{B}, \mathrm{C}, \ldots$ are used to denote the uneven prime factors

of n, and $a, b, c, \dots$ denote, as before, all the prime factors of n. Thus, if n be even, A, B, C, $\dots$ differ from $a, b, c, \dots$ only by the omission of the prime factor 2; and if n be uneven, A, B, C, $\dots$ are identical with $a, b, c, \dots$

Taking, as examples of the formulæ, $n=6$ and $n=9$, we find

$$\Delta_r(6) - 3^r \Delta_r(2) = 1,$$
$$\Delta_r(6) - \Delta_r(3) - \Delta_r(2) + \Delta_r(1) = 0;$$

viz.

$$1^r + 3^r - 3^r = 1,$$
$$1^r + 3^r - 1^r - 3^r - 1^r + 1^r = 0;$$

and

$$\Delta_r(9) - 3^r \Delta_r(3) = 1,$$
$$\Delta_r(9) - \Delta_r(3) = 9^r;$$

viz.

$$1^r + 3^r + 9^r - 3^r(1^r + 3^r) = 1,$$
$$1^r + 3^r + 9^r - 1^r - 3^r = 9^r.$$

If n be uneven, $\Delta_r(n) = \sigma_r(n)$, and the two formulæ are included in those given in the last section. If n be even and $= 2^h m$, where m is uneven, the first formula becomes

$$\sigma_r(m) - \Sigma A^r \sigma_r\left(\frac{m}{A}\right) + \Sigma A^r B^r \sigma_r\left(\frac{m}{AB}\right) - \dots = 1,$$

where A, B, C, $\dots$ are all the prime factors of m; and it is therefore included in the first formula of the last section.

If $r = 0$, $\Delta_r(n)$ denotes the number of the uneven divisors of n. The two formulæ do not coalesce except in the case of n uneven.

Formulæ involving $\Delta_r'(n)$, § 9.

§ $$e_n = n^r, \quad f(x) = \frac{x}{1 - x^2},$$

then

$$F(x) = \frac{x}{1 - x^2} + \frac{2^r x^2}{1 - x^4} + \frac{3^r x^3}{1 - x^6} + \frac{4^r x^4}{1 - x^8} + \&c.$$
$$= x + \Delta_r'(2)x^2 + \Delta_r'(3)x^3 + \Delta_r'(4)x^4 + \&c.,$$

where $\Delta_r'(n)$ denotes the sum of the rth powers of those divisors of n whose conjugates are uneven. Thus we have

$$f(x) = x + \quad x^3 \quad + \quad x^5 \quad + \quad x^7 \quad + \&c.,$$
$$\phi(x) = x + \quad 2^r x^2 \quad + \quad 3^r x^3 \quad + \quad 4^r x^4 \quad + \&c.,$$
$$F(x) = x + \Delta_r'(2)x^2 + \Delta_r'(3)x^3 + \Delta_r'(4)x^4 + \&c.,$$
$$e_n = n^r, \quad \eta_2 = 0, \quad \eta_{2n+1} = 1;$$

whence we find

$$\Delta_r'(n) - \Sigma a^r \Delta_r'\left(\frac{n}{a}\right) + \Sigma a^r b^r \Delta_r'\left(\frac{n}{ab}\right) - \Sigma a^r b^r c^r \Delta_r'\left(\frac{n}{abc}\right) + \dots$$

$$= 0 \text{ or } 1, \text{ according as } n \text{ is even or uneven ;}$$

$$\Delta_r'(n) - \Sigma \Delta_r'\left(\frac{n}{A}\right) + \Sigma \Delta_r'\left(\frac{n}{AB}\right) - \Sigma \Delta_r'\left(\frac{n}{ABC}\right) + \dots = n^r,$$

where A, B, C, ... have the same meaning as in the preceding section.

Taking, as an example, $n = 6$, the formulæ give

$$\Delta_r'(6) - 3^r \Delta_r'(2) - 2^r \Delta_r'(3) + 6^r \Delta_r'(1) = 0,$$

$$\Delta_r'(6) - \Delta_r'(2) = 6^r;$$

viz.

$$2^r + 6^r - 3^r \cdot 2^r - 2^r(1^r + 3^r) + 6^r = 0,$$

$$2^r + 6^r - 2^r = 6^r.$$

If $r = 0$, $\Delta'_r(n)$ denotes the number of divisors of n whose conjugates are uneven.

Formulæ involving $E_r(n)$, § 10.

§ 10. Let $e_2 = 0$ and $e_p = (-1)^{\frac{1}{2}(p-1)} p^r$, where p is any uneven prime, and let $f(x) = \dfrac{x}{1-x}$; then

$$F(x) = \frac{x}{1-x} - \frac{3^r x^3}{1-x^3} + \frac{5^r x^5}{1-x^5} - \frac{7^r x^7}{1-x^7} + \&c.$$

$$= x + E_r(2)x^2 + E_r(3)x^3 + E_r(4)x^4 + \&c.,$$

where $E_r(n)^*$ denotes the excess of the sum of the rth powers of those divisors of n which are of the form $4m + 1$ over the sum of the rth powers of those divisors which are of the form $4m + 3$.

Thus we have

$$f(x) = x + \quad x^2 \quad + \quad x^3 \quad + \quad x^4 + \&c.,$$

$$\phi(x) = x - \quad 3^r x^3 \quad + \quad 5^r x^5 \quad - \quad 7^r x^7 + \&c.,$$

$$F(x) = x + E_r(2)x^2 + E_r(3)x^3 + E_r(4)x^4 + \&c.,$$

$$e_{2n} = 0, \quad e_{2n+1} = (-1)^n(2n+1)^r, \quad \eta_n = 1;$$

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* As there is no risk of confusion between this function $E_r(n)$ and the symbolic operator E_n of §§ 1–3 and 15–20, I have thought it unnecessary to change a notation which I have used in other papers.

whence we find

$$E_r(n) - \Sigma(-1)^{\frac{1}{2}(A-1)}A^r E_r\left(\frac{n}{A}\right) + \Sigma(-1)^{\frac{1}{2}(AB-1)}A^r B^r E_r\left(\frac{n}{AB}\right)$$

$$- \Sigma(-1)^{\frac{1}{2}(ABC-1)}A^r B^r C^r E_r\left(\frac{n}{ABC}\right) + \ldots = 1,$$

$$E_r(n) - \Sigma E_r\left(\frac{n}{a}\right) + \Sigma E_r\left(\frac{n}{ab}\right) - \Sigma E_r\left(\frac{n}{abc}\right) + \ldots$$

$$= 0 \text{ or } (-1)^{\frac{1}{2}(n-1)}n^r, \text{ according as } n \text{ is even or uneven.}$$

If $r = 0$, $E_r(n)$ becomes $E(n)$, the excess of the number of $(4m+1)$ divisors of n over the number of $(4m+3)$ divisors. The function $E(n)$ vanishes when n is of the form $4m+3$, and is never negative.

Formulæ involving $E_r'(n)$, § 11.

§ 11. Let $e_n = n^r$ and $f(x) = \dfrac{x}{1+x^2}$, then

$$F(x) = \frac{x}{1+x^2} + \frac{2^r x^2}{1+x^4} + \frac{3^r x^3}{1+x^6} + \frac{4^r x^4}{1+x^8} + \&c.,$$

$$= x + E_r'(2)x^2 + E_r'(3)x^3 + E_r'(4)x^4 + \&c.;$$

where $E_r'(n)$ denotes the excess of the sum of the rth powers of those divisors of n whose conjugates are of the form $4m+1$ over the sum of the rth powers of those divisors whose conjugates are of the form $4m+3$.

Thus we have

$$f(x) = x - \quad x^3 \quad + \quad x^5 \quad - \quad x^7 \quad + \&c.,$$

$$\phi(x) = x + 2^r x^2 + \quad 3^r x^3 \quad + 4^r x^4 \quad + \&c.,$$

$$F(x) = x + E_r'(2)x^2 + E_r'(3)x^3 + E_r'(4)x^4 + \&c.,$$

$$e_n = n^r, \quad \eta_{2n} = 0, \quad \eta_{2n+1} = (-1)^n;$$

whence we find

$$E_r'(n) - \Sigma a^r E_r'\left(\frac{n}{a}\right) + \Sigma a^r b^r E_r'\left(\frac{n}{ab}\right) - \Sigma a^r b^r c^r E_r'\left(\frac{n}{abc}\right) + \ldots$$

$$= 0 \text{ or } (-1)^{\frac{1}{2}(n-1)}, \text{ according as } n \text{ is even or uneven;}$$

$$E_r'(n) - \Sigma(-1)^{\frac{1}{2}(A-1)}E_r'\left(\frac{n}{A}\right) + \Sigma(-1)^{\frac{1}{2}(AB-1)}E_r'\left(\frac{n}{AB}\right)$$

$$- \Sigma(-1)^{\frac{1}{2}(ABC-1)}E_r'\left(\frac{n}{ABC}\right) + \ldots = n^r.$$

It is easy to see that if n be uneven,

$$E_r'(n) = (-1)^{\frac{1}{2}(n-1)}E_r(n):$$

thus, when n is uneven, these formulæ coincide with those of the preceding section.

The Functions $\sigma_r(n)$, $\Delta_r(n)$, &c., §§ 12, 13.

§ 12. The five functions $\sigma_r(n)$, $\Delta_r(n)$, $\Delta'(n)$, $E_r(n)$, $E_r'(n)$, have been specially considered in the six preceding sections, because, for certain values of r, they occur as coefficients in some of the fundamental q-series in Elliptic Functions. When n is uneven the three functions $\sigma_r(n)$, $\Delta_r(n)$, $\Delta_r'(n)$ become all equal.

The first of the two formulæ in § 6, viz.,

$$\sigma_r(n) - \Sigma\sigma_r\left(\frac{n}{a}\right) + \Sigma\sigma_r\left(\frac{n}{ab}\right) - \ldots = n^r,$$

was given by H. J. S. Smith in vol. vii. p. 211 of the 'Proceedings of the London Mathematical Society'; but so far as I know, no special reference has been made to the other formulæ. All the formulæ may of course be established without the aid of Möbius's theorem; but the duality of the results and their connexion with Möbius's theorem seemed to me to be of interest apart from the results themselves.

It will be observed that the double result is connected with the double form of the q-series in Elliptic Functions. Thus, taking for example the theorem in § 6, in the case of $r=1$, we have $\Sigma_1^\infty \sigma(n)x^n$

$$= \frac{x}{1-x} + \frac{2x^2}{1-x^2} + \frac{3x^3}{1-x^3} + \frac{4x^4}{1-x^4} + \&c.,$$

and, by expanding the terms in rows and summing the columns, we transform this series into

$$\frac{x}{(1-x)^2} + \frac{x^2}{(1-x^2)^2} + \frac{x^3}{(1-x^3)^2} + \frac{x^4}{(1-x^4)^2} + \&c.$$

These two forms of the series correspond to

$$f(x) + e_2 f(x^2) + e_3 f(x^3) + e_4 f(x^4) + \&c.$$

and

$$\phi(x) + \eta_2 \phi(x^2) + \eta_3 \phi(x^3) + \eta_4 \phi(x^4) + \&c.$$

respectively.

In order to apply Möbius's theorem it is unnecessary to actually sum the columns of the developed series, as in the transformation of the q-series.

§ 13. With reference to the quantities e_n (and therefore also η_n), it is to be noticed that they must be such that $e_m \times e_n = e_{mn}$ for all values of m and n. Thus, for example, we cannot put $e_n = (-1)^{n-1}n^r$, viz. $e_n = n^r$ if n be uneven, and $e_n = -n^r$ if n be even, for if $e_2 = -2^r$, we must have

$$e_4 = -2^r \times -2^r = +4^r.$$

The series

$$\frac{x}{1-x} - \frac{2^r x^2}{1-x^2} + \frac{3^r x^3}{1-x^3} - \frac{4^r x^4}{1-x^4} + \text{ &c.,}$$

which occurs in Elliptic Functions, is equal to $\Sigma_1^\infty \zeta_r(n) x^n$, where $\zeta_r(n)$ denotes the excess of the sum of the rth powers of the uneven divisors of n over the sum of the rth powers of the even divisors of n; and we thus see that we do not obtain by Möbius's theorem formulæ involving $\zeta_r(n)$ corresponding to those that have been given in the case of $\mathrm{E}_r(n)$ and $\mathrm{E}_r'(n)$.

It may be remarked that the functions $\sigma_r(n)$, $\Delta_r(n)$, &c. do not satisfy the conditions to which e_n is subject, for the equations $\sigma_r(m) \, \sigma_r(n) = \sigma_r(mn)$, $\Delta_r(m) \, \Delta_r(n) = \Delta_r(mn)$, &c., hold good only when m and n are prime to one another.

Principle of the Method, § 14.

§ 14. The method employed in §§ 6–11 gives a pair of connected theorems relating to a function $\mathrm{P}(n)$, where $\mathrm{P}(n)$ denotes the coefficient of x^n in the expansion of $\mathrm{F}(x)$ in ascending powers of x, viz. if

$$\mathrm{F}(x) = f(x) + e_2 f(x^2) + e_3 f(x^3) + e_4 f(x^4) + \text{ &c.}$$
$$= x + \mathrm{P}(2) x^2 + \mathrm{P}(3) x^3 + \mathrm{P}(4) x^4 + \text{ &c.}$$

and

$$f(x) = x + \eta_2 x^2 + \eta_3 x^3 + \eta_4 x^4 + \text{ &c.,}$$

then

$$\mathrm{P}(n) - \Sigma e_a \mathrm{P}\left(\frac{n}{a}\right) + \Sigma e_{ab} \mathrm{P}\left(\frac{n}{ab}\right) - \Sigma e_{abc} \mathrm{P}\left(\frac{n}{abc}\right) + \ldots = \eta_n,$$

$$\mathrm{P}(n) - \Sigma \eta_a \mathrm{P}\left(\frac{n}{a}\right) + \Sigma \eta_{ab} \mathrm{P}\left(\frac{n}{ab}\right) - \Sigma \eta_{abc} \mathrm{P}\left(\frac{n}{abc}\right) + \ldots = e_n.$$

Development of a certain Symbolic Expression. The Function $\phi(n)$, §§ 15–19.

§ 15. In § 3 the expression

$$\frac{1}{(1 - e_a \mathrm{E}_a)(1 - e_b \mathrm{E}_b)(1 - e_c \mathrm{E}_c)\ldots} f(x)$$

was considered and found to be equal to $\Sigma e_n f(x^n)$, n having all values of the form $a^\alpha b^\beta c^\gamma \ldots$.

We now consider the expression

$$\frac{(1 - \mathrm{E}_a)(1 - \mathrm{E}_b)(1 - \mathrm{E}_c)\ldots}{(1 - e_a \mathrm{E}_a)(1 - e_b \mathrm{E}_b)(1 - e_c \mathrm{E}_c)\ldots} f(x).$$

Since

$$\frac{1 - \mathrm{E}_a}{1 - e_a \mathrm{E}_a} = 1 + (e_a - 1)\mathrm{E}_a + (e_{a^2} - e_a)\mathrm{E}_{a^2} + \text{ &c.,}$$

we see at once that the expression in question is equal to $\Sigma g_n f(x^n)$, where

$$g_n = e_n\left(1 - \frac{1}{e_a}\right)\left(1 - \frac{1}{e_b}\right)\left(1 - \frac{1}{e_c}\right)\ldots,$$

n having the same values as before, and a, b, c, ... being the prime factors of n.

§ 16. If $e_n = n$, then

$$g_n = n\left(1 - \frac{1}{a}\right)\left(1 - \frac{1}{b}\right)\left(1 - \frac{1}{c}\right)\ldots$$

This is the well-known expression for the number of numbers less than n and prime to it. Adopting Gauss's notation and denoting this quantity by $\phi(n)$, we thus obtain the result :—

$$\frac{(1 - E_2)(1 - E_3)(1 - E_5)\ldots}{(1 - 2E_2)(1 - 3E_3)(1 - 5E_5)\ldots} f(x)$$
$$= f(x) + \phi(2)f(x^2) + \phi(3)f(x^3) + \phi(4)f(x^4) + \&c.$$

§ 17. As a particular case of this theorem, let

$$f(x) = \frac{x}{1 - x};$$

we thus find

$$\frac{(1 - E_2)(1 - E_3)(1 - E_5)\ldots}{(1 - 2E_2)(1 - 3E_3)(1 - 5E_5)\ldots} \frac{x}{1 - x}$$
$$= \frac{x}{1 - x} + \frac{\phi(2)x^2}{1 - x^2} + \frac{\phi(3)x^3}{1 - x^3} + \frac{\phi(4)x^4}{1 - x^4} + \&c.$$

Now

$$\frac{1}{(1 - 2E_2)(1 - 3E_3)(1 - 5E_5)\ldots} \frac{x}{1 - x}$$
$$= \frac{x}{1 - x} + \frac{2x^2}{1 - x^2} + \frac{3x^3}{1 - x^3} + \frac{4x^4}{1 - x^4} + \&c.$$
$$= x + \sigma(2)x^2 + \sigma(3)x^3 + \sigma(4)x^4 + \&c.;$$

and, operating on this series with

$$(1 - E_2)(1 - E_3)(1 - E_5)\ldots,$$

we obtain as result

$$\Sigma_1^\infty \sigma(n)x^n - \Sigma_1^\infty \sigma(n)x^{2n} - \Sigma_1^\infty \sigma(n)x^{3n}$$
$$- \Sigma_1^\infty \sigma(n)x^{5n} + \Sigma_1^\infty \sigma(n)x \quad - \&c.$$

Also it is evident that

$$(1 - E_2)(1 - E_3)(1 - E_5)\ldots \frac{x}{1 - x} = x;$$

and, operating on x by

$$\frac{1}{(1-2E_2)(1-3E_3)(1-5E_5)\ldots},$$

we obtain as result

$$x+2x^2+3x^3+4x^4+ \&c.,$$

which

$$=\frac{x}{(1-x)^2}.$$

§ 18. We have thus found for the expression

$$\frac{(1-E_2)(1-E_3)(1-E_5)\ldots}{(1-2E_2)(1-3E_3)(1-5E_5)\ldots}\ \ \frac{x}{1-x}$$

the three results :—

(i.) $\Sigma_1^\infty \dfrac{\phi(n)x^n}{1-x^n},$

(ii.) $\Sigma_1^\infty \sigma(n)x^n - \Sigma_1^\infty \sigma(n)x^{2n} - \Sigma_1^\infty \sigma(n)x^{3n} - \&c.,$

(iii.) $\dfrac{x}{(1-x)^2},$

the first being obtained by operating with the operator as a whole, the second by operating first with the denominator, and the third by operating first with the numerator.

By equating the coefficients of x^n in these three expressions, we find that

$$\phi(1)+\phi(f)+\phi(g)+\phi(h)\ldots \ \ +\phi(n),$$

and

$$\sigma(n)-\Sigma\sigma\left(\frac{n}{a}\right)+\Sigma\sigma\left(\frac{n}{ab}\right)-\Sigma\sigma\left(\frac{n}{abc}\right)+\ldots$$

are each equal to n, where $1, f, g, h, \ldots \ldots n$ denote all the divisors of n.

The first result, viz. that

$$\phi(1)+\phi(f)+\phi(g)\ldots \ \ +\phi(n)=n,$$

was given by Gauss in § 39 of the *Disquisitiones Arithmeticæ*. The second result is the particular case $r=1$ of the second of the two formulæ proved in § 6.

It is curious that two theorems so distinct in character should be derivable by means of different developments of the same operator. The symbolic expression for the series $\Sigma_1^\infty \phi(n)f(x^n)$ seems also deserving of notice.

§ 19. It will be observed that the processes of the three preceding sections are equally applicable if we put $e_n = n^r$,

instead of n; and that if $\phi(n)$ be a quantity defined by the equation

$$\phi_r(n) = n^r\Big(1 - \frac{1}{a}\Big)\Big(1 - \frac{1}{b^r}\Big)\Big(1 - \frac{1}{c^r}\Big)\ldots,$$

we find

$$\phi_r(1) + \phi^r(f) + \phi_r(g) + \phi(h)\ldots \quad + \phi_r(n)$$
$$= \sigma_r(n) - \Sigma\sigma_r\Big(\frac{n}{a}\Big) + \Sigma\sigma_r\Big(\frac{n}{ab}\Big) - \Sigma\sigma_r\Big(\frac{n}{abc}\Big) + \ldots$$
$$= n^r.$$

Second formula involving $\phi(n)$, §§ 20, 21.

§ 20. From the formula proved in § 16 it follows that

$$(1 - 2E_2)(1 - 3E_3)(1 - 5E_5)\ldots\Sigma_1^{\infty}\phi(n)f(x^n)$$
$$= (1 - E_2)(1 - E_3)(1 - E_5)\ldots f(x),$$

and by equating the coefficients of $f(x^n)$ in this equation we obtain the formula

$$\phi(n) - \Sigma a\phi\Big(\frac{n}{a}\Big) + \Sigma ab\phi\Big(\frac{n}{ab}\Big) - \Sigma abc\phi\Big(\frac{n}{abc}\Big) + \ldots$$
$$= 0 \text{ or } (-1)^{\mathrm{N}},$$

according as n is divisible by a squared factor or is the product of N simple prime factors. Thus, for example, putting $n = 10$, 20 and 30, the formula gives

$$\phi(10) - 2\phi(5) \quad -5\phi(2) + 10\phi(1) = 1,$$
$$\phi(20) - 2\phi(10) - 5\phi(4) + 10\phi(2) = 0,$$
$$\phi(30) - 2\phi(15) - 3\phi(10) - 5\phi(6) + 6\phi(5) + 10\phi(3) + 15\phi(2)$$
$$\quad - 30\phi(1) = -1,$$

viz.

$$4 - 8 - 5 + 10 = 1,$$
$$8 - 8 - 10 + 10 = 0,$$
$$8 - 16 - 12 - 10 + 24 + 20 + 15 - 30 = -1.$$

§ 21. In a similar manner we find that

$$\phi_r(n) - \Sigma a^r\phi_r\Big(\frac{n}{a}\Big) + \Sigma a^r b^r\phi_r\Big(\frac{n}{ab}\Big) - \Sigma a^r b^r c^r\phi_r\Big(\frac{n}{abc}\Big) + \ldots$$

$$= 0 \text{ or } (-1)^{\mathrm{N}}, \text{ according as } n \text{ is divisible by a squared}$$

factor or is the product of N simple prime factors.

Expressions for $\sigma_r(n)$, $\Delta_r(n)$, &c. as Determinants, §§ 22–28.
Expressions for $\sigma(n)$, § 22.

§ 22. From the formulæ of §§ 6–11 we may readily deduce expressions for $\sigma_r(n)$ &c. as determinants of n rows.

Thus taking, for example, the formulæ of § 6 in the case of $r=1$, we have

$$\sigma(1)=1$$
$$\sigma(2)-\sigma(1)=2$$
$$\sigma(3)\qquad-\sigma(1)=3$$
$$\sigma(4)\qquad-\sigma(2)\qquad=4$$
$$\sigma(5)\qquad\qquad-\sigma(1)=5$$
$$\sigma(6)\qquad-\sigma(3)-\sigma(2)+\sigma(1)=6$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

and

$$\sigma(1)=1$$
$$\sigma(2)-2\sigma(1)=1$$
$$\sigma(3)\qquad-3\sigma(1)=1$$
$$\sigma(4)\qquad-2\sigma(2)\qquad=1$$
$$\sigma(5)\qquad\qquad-5\sigma(1)=1$$
$$\sigma(6)\qquad-2\sigma(3)-3\sigma(2)+6\sigma(1)=1$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

From the first system of equations we find:—

(i.)

$$\sigma(n)=(-)^{n-1}\begin{vmatrix} 1, & 2, & 3, & 4, & 5, & 6,\ldots \\ 1, & -1, & -1, & 0, & -1, & 1,\ldots \\ 0, & 1, & 0, & -1, & 0, & -1,\ldots \\ 0, & 0, & 1, & 0, & 0, & -1,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

And from the second system:—

(ii.)

$$\sigma(n)=(-)^{n-1}\begin{vmatrix} 1, & 1, & 1, & 1, & 1, & 1,\ldots \\ 1, & -2, & -3, & 0, & -5, & 6,\ldots \\ 0, & 1, & 0, & -2, & 0, & -3,\ldots \\ 0, & 0, & 1, & 0, & 0, & -2,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

In the first determinant the first row consists of the natural numbers; the second row is formed by entering 1

if the corresponding number in the first row is the simple product of an even number of different primes, −1 if it is the simple product of an uneven number of different primes, and 0 if it contains a squared factor. The third row is formed by dividing the numbers in the first row by 2, and entering, under those which are so divisible, 1, −1, or 0, according as the quotient consists of the simple product of an even or uneven number of different primes or contains a squared factor. The fourth row is formed in the same manner, the divisor being 3; and so on. The spaces left blank are to be filled in with ciphers. The number unity is to be regarded as the product of an even number of primes, *i. e.* corresponding to the quotient unity, 1 is to be entered.

In the second determinant the ciphers and the signs of the elements are the same as in the first determinant; but the actual quotients themselves are entered, and each element in the first row is replaced by unity.

Both determinants are of the *n*th order.

Expressions for $\sigma_r(n)$, § 23.

§ 23. Proceeding in the same manner and using the general formulæ of § 6, we find :—

(i.)

$$\sigma_r(n)=(-)^{n-1}\begin{vmatrix} 1^r, & 2^r, & 3^r, & 4^r, & 5^r, & 6^r, \ldots \\ 1, & -1, & -1, & 0, & -1, & 1, \ldots \\ 0, & 1, & 0, & -1, & 0, & -1, \ldots \\ 0, & 0, & 1, & 0, & 0, & -1, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix},$$

this determinant differing from the first determinant for $\sigma(n)$ only in the first row, the elements of which are raised to the power *r*; and also:—

(ii.)

$$\sigma_r(n)=(-)^{n-1}\begin{vmatrix} 1, & 1, & 1, & 1, & 1, & 1, \ldots \\ 1^r, & -2^r, & -3^r, & 0, & -5^r, & 6^r, \ldots \\ 0, & 1^r, & 0, & -2^r, & 0, & -3^r, \ldots \\ 0, & 0, & 1^r, & 0, & 0, & -2^r, \ldots \\ 0, & 0, & 0, & 1^r, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1^r, & 0, \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

This determinant may be derived from the second determinant for $\sigma(n)$ by replacing every element $\pm m$ by $\pm m^r$.

Expression for $\nu(n)$, § 24.

§ 24. Putting $r=0$ in either of the determinants of the preceding section, we find:—

$$\nu(n)=(-)^{n-1}\begin{vmatrix} 1, & 1, & 1, & 1, & 1, & 1,\ldots \\ 1, & -1, & -1, & 0, & -1, & 1,\ldots \\ 0, & 1, & 0, & -1, & 0, & -1,\ldots \\ 0, & 0, & 1, & 0, & 0, & -1,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

Expressions for $\Delta_r(n)$, § 25.

§ 25. The formulæ of § 8 lead to the following determinant-expressions for $\Delta_r(n)$:—

(i.)

$$\Delta_r(n)=(-)^{n-1}\begin{vmatrix} 1^r, & 0, & 3^r, & 0, & 5^r, & 0,\ldots \\ 1, & -1, & -1, & 0, & -1, & 1,\ldots \\ 0, & 1, & 0, & -1, & 0, & -1,\ldots \\ 0, & 0, & 1, & 0, & 0, & -1,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

This determinant may be derived from the first determinant for $\sigma_r(n)$ by replacing the elements which involve even numerals in the first row by zeros.

(ii.)

$$\Delta_r(n)=(-)^{n-1}\begin{vmatrix} 1, & 1, & 1, & 1, & 1, & 1,\ldots \\ 1^r, & 0, & -3^r, & 0, & -5^r, & 0,\ldots \\ 0, & 1^r, & 0, & 0, & 0, & -3^r,\ldots \\ 0, & 0, & 1^r, & 0, & 0, & 0,\ldots \\ 0, & 0, & 0, & 1^r, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1^r, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

This determinant may be derived from the second determinant for $\sigma_r(n)$ by replacing every element involving even numerals by zero.

Expressions for $\Delta_r'(n)$, § 26.

§ 26. The corresponding expressions for $\Delta_r'(n)$ are:—

(i.)

$$\Delta_r'(n) = (-)^{n-1} \begin{vmatrix} 1^r, & 2^r, & 3^r, & 4^r, & 5^r, & 6^r, \ldots \\ 1, & 0, & -1, & 0, & -1, & 0, \ldots \\ 0, & 1, & 0, & 0, & 0, & -1, \ldots \\ 0, & 0, & 1, & 0, & 0, & 0, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

Excepting only the first line, the elements of this determinant may be derived from those of the second determinant for $\Delta_r(n)$ by putting $r=0$.

(ii.)

$$\Delta_r'(n) = (-)^{n-1} \begin{vmatrix} 1, & 0, & 1, & 0, & 1, & 0, \ldots \\ 1, & -2^r, & -3^r, & 0, & -5^r, & 6^r, \ldots \\ 0, & 1^r, & 0, & -2^r, & 0, & -3^r, \ldots \\ 0, & 0, & 1^r, & 0, & 0, & -2^r, \ldots \\ 0, & 0, & 0, & 1^r, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1^r, & 0, \ldots \\ & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

This determinant differs from the second determinant for $\sigma_r(n)$ only in the first row, which consists of 1 and 0 alternately.

Expressions for $\mathrm{E}_r(n)$, § 27.

§ 27. For $\mathrm{E}(n)$ we obtain the expressions:—

(i.)

$$\mathrm{E}_r(n) = (-)^{n-1} \begin{vmatrix} 1^r, & 0, & -3^r, & 0, & 5^r, & 0, \ldots \\ 1, & -1, & -1, & 0, & -1, & 1, \ldots \\ 0, & 1, & 0, & -1, & 0, & -1, \ldots \\ 0, & 0, & 1, & 0, & 0, & -1, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

The mth element of the first row is 0 or $(-1)^{\frac{1}{2}(m-1)}m^r$

according as m is even or uneven. The rest of the determinant is the same as in the first determinant for $\sigma_r(n)$.

$$(\text{ii.})$$

$$E_r(n) = (-)^{n-1} \begin{vmatrix} 1, & 1, & 1, & 1, & 1, & 1, \ldots \\ 1^r, & 0, & 3^r, & 0, & -5^r, & 0, \ldots \\ 0, & 1^r, & 0, & 0, & 0, & 3^r, \ldots \\ 0, & 0, & 1^r, & 0, & 0, & 0, \ldots \\ 0, & 0, & 0, & 1^r, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1^r, & 0, \ldots \\ . & . & . & . & . & . & . & . & . \end{vmatrix}$$

This determinant may be derived from the second determinant for $\Delta_r(n)$ by changing the sign of every element $\pm s^r$, in which s is of the form $4m+3$.

Expressions for $E_r'(n)$, § 28.

§ 28. For $E_r'(n)$ we obtain the expressions :—

$$(\text{i.})$$

$$E_r'(n) = (-)^{n-1} \begin{vmatrix} 1^r, & 2^r, & 3^r, & 4^r, & 5^r, & 6^r, \ldots \\ 1, & 0, & 1, & 0, & -1, & 0, \ldots \\ 0, & 1, & 0, & 0, & 0, & 1, \ldots \\ 0, & 0, & 1, & 0, & 0, & 0, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ . & . & . & . & . & . & . & . & . \end{vmatrix}$$

Excepting the first row, this determinant may be derived from the second determinant for $E_r(n)$ by putting $r=0$.

$$(\text{ii.})$$

$$E_r'(n) = (-)^{n-1} \begin{vmatrix} 1, & 0, & -1, & 0, & 1, & 0, \ldots \\ 1^r, & -2^r, & -3^r, & 0, & -5^r, & 6^r, \ldots \\ 0, & 1^r, & 0, & -2^r, & 0, & -3^r, \ldots \\ 0, & 0, & 1, & 0, & 0, & -2^r, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ . & . & . & . & . & . & . & . & . \end{vmatrix}$$

The mth element of the first row is 0 or $(-1)^{\frac{1}{2}(m-1)}$, according as m is even or uneven; the rest of the determinant is the same as in the second determinant for $\sigma_r(n)$.

Expressions for $\phi(n)$, § 29.

§ 29. From Gauss's formula (§ 18) and the formula of § 20, we find

$$\phi(1)=1$$
$$\phi(2)+\phi(1)=2$$
$$\phi(3)\qquad+\phi(1)=3$$
$$\phi(4)\qquad+\phi(2)+\phi(1)=4$$
$$\phi(5)\qquad\qquad+\phi(1)=5$$
$$\phi(6)\qquad+\phi(3)+\phi(2)+\phi(1)=6$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

and

$$\phi(1)=\quad 1$$
$$\phi(2)-2\phi(1)=-1$$
$$\phi(3)\qquad-3\phi(1)=-1$$
$$\phi(4)\qquad-2\phi(2)\qquad=\quad 0$$
$$\phi(5)\qquad\qquad-5\phi(1)=-1$$
$$\phi(6)\qquad-2\phi(3)-3\phi(2)+6\phi(1)=\quad 1$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

The first system of equations gives:—

$$\phi(n)=(-)^{n-1}\begin{vmatrix} 1, & 2, & 3, & 4, & 5, & 6,\ldots \\ 1, & 1, & 1, & 1, & 1, & 1,\ldots \\ 0, & 1, & 0, & 1, & 0, & 1,\ldots \\ 0, & 0, & 1, & 0, & 0, & 1,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\;\cdot\;\cdot \end{vmatrix}$$

where in the third row every alternate element is unity, in the fourth row every third element is unity, and so on.

The second system of equations gives:—

$$\phi(n)=(-)^{n-1}\begin{vmatrix} 1, & -1, & -1, & 0, & -1, & 1,\ldots \\ 1, & -2, & -3, & 0, & -5, & 6,\ldots \\ 0, & 1, & 0, & -2, & 0, & -3,\ldots \\ 0, & 0, & 1, & 0, & 0, & -2,\ldots \\ 0, & 0, & 0, & 1, & 0, & 0,\ldots \\ 0, & 0, & 0, & 0, & 1, & 0,\ldots \\ \cdot & \cdot & \cdot & \cdot\;\cdot & \cdot & \cdot\;\cdot\;\cdot \end{vmatrix}$$

where the mth element of the first row is 0 or $(-1)^M$ according as m is divisible by a squared factor or is the product of M simple prime factors; and the rest of the determinant is the same as in the second determinant for $\sigma(n)$ in § 22.

Expressions for $\phi_r(n)$, § 30.

§ 30. Similarly we find from §§ 19 and 21 that

(i.)

$$\phi_r(n)=(-)^{n-1}\begin{vmatrix} 1^r, & 2^r, & 3^r, & 4^r, & 5^r, & 6^r, \ldots \\ 1, & 1, & 1, & 1, & 1, & 1, \ldots \\ 0, & 1, & 0, & 1, & 0, & 1, \ldots \\ 0, & 0, & 1, & 0, & 0, & 1, \ldots \\ 0, & 0, & 0, & 1, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1, & 0, \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

(ii.)

$$\phi_r(n)=(-)^{n-1}\begin{vmatrix} 1, & -1, & -1, & 0, & -1, & 1, \ldots \\ 1, & -2^r, & -3^r, & 0, & -5^r, & 6^r, \ldots \\ 0, & 1^r, & 0, & -2^r, & 0, & -3^r, \ldots \\ 0, & 0, & 1^r, & 0, & 0, & -2^r, \ldots \\ 0, & 0, & 0, & 1^r, & 0, & 0, \ldots \\ 0, & 0, & 0, & 0, & 1^r, & 0, \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

In all the determinants the number of rows is supposed to be n.

The Determinant-Expressions, § 31.

§ 31. The preceding determinant-expressions for $\sigma_r(n)$ &c. are of course of no practical value, and they would be much less convenient for purposes of calculation than the systems of equations which they represent. Indeed, since in order to form the determinants, it is requisite to divide not only n but also every number less than n by all its divisors, it is clear that it would be much simpler to obtain the values of $\sigma(n)$ &c. directly from their definitions. The determinant-expressions are, however, of some theoretical interest as affording definite numerical expressions for $\sigma(n)$ &c.

Conversely we may regard the results of §§ 22–28 as affording evaluations of the determinants themselves, these determinants being of some interest on account of the curious law of their formation. Regarding the formulæ from this point of view, it may be noticed that case (i.) of Möbius's theorem (§ 4) implies that the determinant

$$
\begin{vmatrix}
2^r, & 3^r, & 4^r, & 5^r, & 6^r, \ldots, & n^r \\
1^r, & 0, & 2^r, & 0, & 3^r, \ldots, & \\
0, & 1^r, & 0, & 0, & 2^r, \ldots, & \\
0, & 0, & 1^r, & 0, & 0, \ldots, & \\
0, & 0, & 0, & 1^r, & 0, \ldots, & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot \quad \cdot \quad \cdot, \\
0, & 0, & 0, & 0, & 0, \ldots, & 1^r
\end{vmatrix}
$$

$= 0$ or $(-1)^{n+N-1} n^r$, according as n is divisible by a squared factor or is the product of N simple primes. The second row of the determinant is derived from the first by division by 2^r, the third by division by 3^r, and so on. Similarly case (ii.) implies that

$$
\begin{vmatrix}
3^r, & 5^r, & 7^r, & 9^r, & 11^r, \ldots & (2n+1)^r \\
1^r, & 0, & 0, & 3^r, & 0, \ldots, & \\
0, & 1^r, & 0, & 0, & 0, \ldots, & \\
0, & 0, & 1^r, & 0, & 0, \ldots, & \\
0, & 0, & 0, & 1^r, & 0, \ldots, & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot \quad \cdot \quad \cdot, \\
0, & 0, & 0, & 0, & 0, \ldots, & 1^r
\end{vmatrix}
$$

$= 0$ or $(-)^{n+N} (2n+1)^r$, according as $2n+1$ is divisible by a squared factor or is the product of N simple primes.

Application of the Theorem to Elliptic Functions, § 32.

§ 32. Most of the q-series in Elliptic Functions are of the form

$$
f(q) + e_2 f(q^2) + e_3 f(q^3) + e_4 f(q^4) + \&c. = F(k, k', K);
$$

and if we denote by k_n, k_n', K_n the quantities into which k, k', K are transformed by the change of q into q^n, we may deduce from such a series a formula of the form

$$
f(q) = F(k, k', K) - e_2 F(k_2, k'_2, K_2) - e_3 F(k_3, k'_3, K_3) \\
- e_5 F(k_5, k'_5, K_5) + e_6 F(k_6, k'_6, K_6) - \ldots
$$

Results of this kind do not appear to be of any great interest, but it may be remarked that as we may obtain in this manner several expressions for the same quantity $f(q)$, we are thus led to certain equalities between elliptic-functions expressions in which the terms are subject to Möbius's law.

Thus, for example, from the formula

$$\frac{2k\mathrm{K}}{\pi} = 4\sum_1^\infty \frac{q^{\frac{1}{2}(2n-1)}}{1+q^{2n-1}}$$

we find

$$\frac{2q^{\frac{1}{2}}}{1+q} = \frac{1}{\pi}\left\{k\mathrm{K} - k_3\mathrm{K}_3 - k_5\mathrm{K}_5 - k_7\mathrm{K}_7 - k_{11}\mathrm{K}_{11} - \&\mathrm{c.}\right\};$$

and from the formula

$$k\left(\frac{2\mathrm{K}}{\pi}\right)^3 = 4\sum_1^\infty \frac{(2n-1)^2 q^{\frac{1}{2}(2n-1)}}{1+q^{2n-1}}$$

we find

$$\tfrac{1}{2}\frac{q^{\frac{1}{2}}}{1+q} = \frac{1}{\pi^3}\left\{k\mathrm{K}^3 - 3^2 k_3\mathrm{K}_3^3 - 5^2 k_5\mathrm{K}_5^3 - 7^2 k_7\mathrm{K}_7^3 - 11^2 k_{11}\mathrm{K}_{11}^3 - \&\mathrm{c.}\right\}.$$

From these two results it follows that

$$k\mathrm{K}^3 - 3^2 k_3\mathrm{K}_3^3 - 5^2 k_5\mathrm{K}_5^3 - 7^2 k_7\mathrm{K}_7^3 - \&\mathrm{c.}$$
$$= \tfrac{1}{4}\pi^2(k\mathrm{K} - k_3\mathrm{K}_3 - k_5\mathrm{K}_5 - k_7\mathrm{K}_7 - \&\mathrm{c.}).$$

Similarly, since

$$\frac{2k\mathrm{K}}{\pi} = 4\sum_1^\infty (-)^{n-1}\frac{q^{\frac{1}{2}(2n-1)}}{1-q^{2n-1}},$$

and

$$kk'^2\left(\frac{2\mathrm{K}}{\pi}\right)^3 = 4\sum_1^\infty (-)^{n-1}\frac{(2n-1)^2 q^{\frac{1}{2}(2n-1)}}{1-q^{2n-1}},$$

we find

$$\frac{q^{\frac{1}{2}(2n-1)}}{1-q^{2n-1}} = \frac{1}{2\pi}\left\{k\mathrm{K} + k_3\mathrm{K}_3 - k_5\mathrm{K}_5 + k_7\mathrm{K}_7 + k_{11}\mathrm{K}_{11} - k_{13}\mathrm{K}_{13} - \&\mathrm{c.}\right\}$$

$$= \frac{2}{\pi^3}\left\{kk'^2\mathrm{K}^3 + 3^2 k_3 k_3'^2\mathrm{K}_3 - 5^2 k_5 k_5'^2\mathrm{K}_5 + 7^2 k_7 k_7'^2\mathrm{K}_7 + \&\mathrm{c.}\right\}.$$

LIX. *Notices respecting New Books.*

The Advanced Part of a Treatise on the Dynamics of a System of Rigid Bodies, being Part II. of a Treatise on the whole subject; with numerous examples. By E. J. ROUTH, *D.Sc., F.R.S.* London: Macmillan and Co. 1884. (Pp. xii+343.)

THIRTY years ago the text-book at Cambridge on this subject was usually a work which was professedly little more than a Syllabus, consisting of 88 pages of text and 28 pages of examples. It was expected that the student's reading should be supplemented by oral teaching both of College lectures and of the private "coach." Now "the subject is so vast and has so many applications, that a small book can only be made by omitting or treating imperfectly some of its details." These are the words of our author, than whom hardly any one at the present time can speak with greater authority on this branch of Mathematics.

The general scope of the treatise in this its "fourth edition, revised and enlarged," was indicated by us in our notice of the first part (Phil. Mag. March 1883); and little more is needed than for us to state what portions of the subject Dr. Routh has handled in this second part. These are discussed under thirteen chapters, respectively headed :—Moving axes and relative motion ; oscillations about equilibrium, and about a state of motion ; motion of a body under the action of no forces and under any forces ; nature of the motion given by linear equations, and the conditions of stability ; free and forced oscillations : determinations of the constants of integration in terms of the initial conditions ; applications of the Calculus of Finite Differences, and of the Calculus of Variations ; Precession and Nutation ; motion of a string or chain ; and motion of a membrane. It will thus be seen that there is much new matter ; though, on the other hand, there is, of course, much which found a place in the third edition ; but in the last-cited edition we have 564 pages to set against 385+343 pages in this fourth edition. The whole, on perusal, will, however, be found to have been carefully recast, and quite a number of illustrative problems have been added and discussed. The author has not only long worked at his subject, but has been working at it up to the present date. These recent results, which first saw the light in the 'Proceedings of the London Mathematical Society,' have been incorporated here, but in a somewhat different guise ; even results published so lately as in the closing numbers of the Society's present volume of 'Proceedings' find a place (see p. 243).

Dr. Routh has again introduced a few historical notes, which we are always pleased to come across in a text-book, and has removed from an Appendix to a place in the early part (pp. 108, 109) his interesting ("they appear to be new") properties of the spheroconic or spherical ellipse. In addition we have some illustrations from the game of billiards ("to supply some results which may be submitted to experiment"), and much light is, by the way, thrown upon (if also derived from) numerous branches of Analysis. The book appears to be very accurately printed ; at any rate there are

no printers' mistakes which are manifest upon an ordinary examination, possibly a working student may be able to detect a few errata. Should a new edition be called for, it would not now be a difficult matter to draw up an index. It gives one an idea of the detail with which mathematical subjects are now treated when an index to a text-book is suggested as an almost indispensable adjunct.

LX. *Intelligence and Miscellaneous Articles.*

ON THE ELECTRICAL CONDUCTIVITY OF WATER DISTILLED IN VACUO. BY F. KOHLRAUSCH.

THE question of the electrical conductivity of water is not yet settled. By a number of precautions, and by particular care in the preparation and conservation of water, I succeeded in obtaining it with a conductivity at 22° of only 72 billionths of that of mercury*. But even if this, or an adjacent value, was repeatedly the lowest attainable limit in various distillations, it could not be maintained that it really represents the conductivity of water, for the preparation of perfectly pure water in the ordinary way seems bound up with insuperable difficulties.

One of the difficulties consists probably in the influence of air in the distillation. Just as in rain-water compounds of nitrogen, hydrogen, and oxygen, for instance nitrite of ammonia, have been found, so also even in artificial distillation traces of similar products might occur.

It is also possible that the mere absorption of air produces the conductivity or, at all events, increases it. On the same occasion I showed that electrolytes got their conductivity mainly by admixture, and thus the addition of a gas, even if it itself does not conduct, might exert an influence. The investigation of this question with the air-pump failed at that time in consequence of other errors thereby introduced.

It is found, in fact, that the distillation of water in vacuum leads to a far smaller conductivity than that previously found.

A distilling apparatus in the nature of a water, however, is comparatively easy to construct. A glass vessel of 100 to 200 c. c. capacity, which is to serve as retort, is connected by a glass tube with a smaller vessel, which is provided with two platinized electrodes, each of about 5 square centimetres surface. The resistance of the latter vessel, when filled to various heights, was ascertained by means of an extremely dilute solution of sal ammoniac, the resistance of which was known independently. The vessels were then carefully washed out.

By a still open tube the two connected vessels were supplied with a suitable quantity of what was already very pure water; the tube was connected with the mercurial pump, and the water allowed to boil in its vacuum, and when the boiling ceased it was allowed to evaporate at a moderate temperature for about a quarter of an hour, with frequent shaking. Cooled sulphuric acid absorbed

* Pogg. *Ann.* vol. clix. p. 270.

the aqueous vapour. In order to be able to shake the distilling apparatus with its water briskly, the connexion with the mercurial air-pump was made in the manner described by Kundt, that is by means of long bent glass tubes. The supply-tube already mentioned was hermetically sealed. Mr. Otto Wiegand, of Wurzburg, the glass-blower, who had also constructed the double vessel, gave his experienced help in these operations.

The vacuum thus obtained I estimate at 0·01 mm. pressure at most.

There is so much water in the apparatus, that when it is brought into the larger vessel it is two-thirds full. By using a moderately warm hot-air bath of 30° to 45°, and a cooling bath between 0° and −8°, there being no freezing on account of the heat of condensation, the requisite quantity of 6 to 8 c. c. was distilled over into the resistance vessel. This took from 8 to 15 minutes, according to circumstances.

The capacity of the two apparatus was only about 0·00002 Siemens unit. The water had up to a resistance of 80,000 units. From the small delicacy of the dynamometer or of the telephone under these circumstances, alternating currents were not used, but short separate throws with an extremely sensitive rapidly vibrating galvanometer in the bridge. Two Smee's elements produced the current. With careful treatment great electrolytic resistances of this kind may be determined with sufficient accuracy. The current is so weak that the polarization requires a few tenths of a second. By using a varying number of elements, by occasionally reversing the current, and by varying the duration, an accuracy of one to two per cent. could be obtained.

Even in a vacuum the resistance of a distillate was not constant, but diminished with the time. In one of the vessels this decrease was even considerable, so that the resistance of a distillate, which 5 minutes after ending the distillation was 660,000 ohms, sank after 10 minutes to 337,000, in 1 hour to 236,000, in 3 hours to 84,000, and in 15 hours to 26,400, that is $\frac{1}{25}$ of the first value. The initial increase of conductivity is almost uniform. Whether this action is due to the sides of the glass vessel or to the platinum electrodes, I cannot at present say. In the other vessel the resistance decreased more slowly.

In any case it is necessary to hasten with the measurement of resistance after the distillation is complete, so that the temperature, whether judged by the feel or by using a bath, is only approximately determined.

Eight different distillations gave the following conducting powers as compared with mercury, to which are prefixed the temperature and the number of minutes that have elapsed since the end of the distillation.

Vessel I.			Vessel II.		
°	Min.		°	Min.	
20	3	$29 \cdot 10^{-12}$	16	3	$29 \cdot 10^{-12}$
12	2	25 ,,	18	4	28 ,,
20	3	32 ,,	20	3	27 ,,
8	2	25 ,,	20	4	31 ,,

The experiments lead therefore in all cases to conductivities which are not greatly different. The smaller numbers are the more important, for no circumstances can be conceived which make the conducting power appear too small.

From the time which elapses during and since the distillation the numbers are in any case too large. An impartial consideration would deduce from them for the conductivity of water 0·000000000025, or 1/40-milliardth of that of mercury; so that a thread of water 1 mm. in length has the same resistance as a thread of mercury of the same thickness which encircles the earth.

According to this the resistance of an ohm is represented by a layer of water with a cross section of 1 square millim. and a length of about the 26 billionths of a millimetre. The "water-unit of resistance"—a column of water a metre in length and a square millimetre in cross section—has almost a resistance of $4·10^{10}$ ohms. To produce the same resistance a copper wire a millimetre square must have a length of $24·10^8$ kilometres, a distance which light would traverse in about 2·2 hours. If a semicircular electrode a metre in diameter were sunk in the surface of a large mass of water, the resistance would amount to about 12,000 ohms.

A body with so small a conductivity may in many cases be considered a non-conductor for voltaic electricity.

Distillation *in vacuo*, as described above, has had the very satisfactory result of leading by a far simpler method to a conductivity almost one third of that previously found, or, as we may say with some justification, to a water three times as pure.

All that can be maintained with certainty is that the conductivity given above is again an upper limit.—*Berichte der Akad. der Wissenschaften zu Berlin*, Oct. 23, 1884.

ON THE COEFFICIENT OF FRICTION OF GASES AND VAPOURS, AND THEIR DEPENDENCE ON TEMPERATURE. BY O. SCHUMANN.

The conclusions drawn by the author from a long series of experiments are as follows :—

1. Maxwell's formula gives, for a different arrangement of the experiments, values for the coefficient of friction which show greater deviations from each other than would correspond to errors of observation, and this is particularly the case with high temperatures.

2. By introducing a correction into Maxwell's formula, numbers are obtained which, at ordinary temperature, exhibit a close agreement with the method of transpiration.

3. Owing to absorption, the method of transpiration gives too high values of the coefficient of friction. With vapours the values are too small for the same reason.

4. The dependence of the coefficient of friction on the temperature increases with the temperature.

5. The coefficients of all the vapours examined by me have almost the same function of temperature.

6. The relation found by Puluj to exist between length of path and refractive index holds for the vapours of homologous ethers at corresponding temperatures.—Wiedemann's *Annalen*, Nov. 1884.

INDEX TO VOL. XVIII.

END OF THE EIGHTEENTH VOLUME.

DIAGRAM OF THE MELTING POINTS OF THE
NORMAL CHLORIDES, BROMIDES & IODIDES
OF THE ELEMENTS.

Chlorides, ————————
Bromides, ————————
Iodides, - - - - - - - - -

Melting Point (Measured from −273° C.)

Atomic Weight of Positive Element
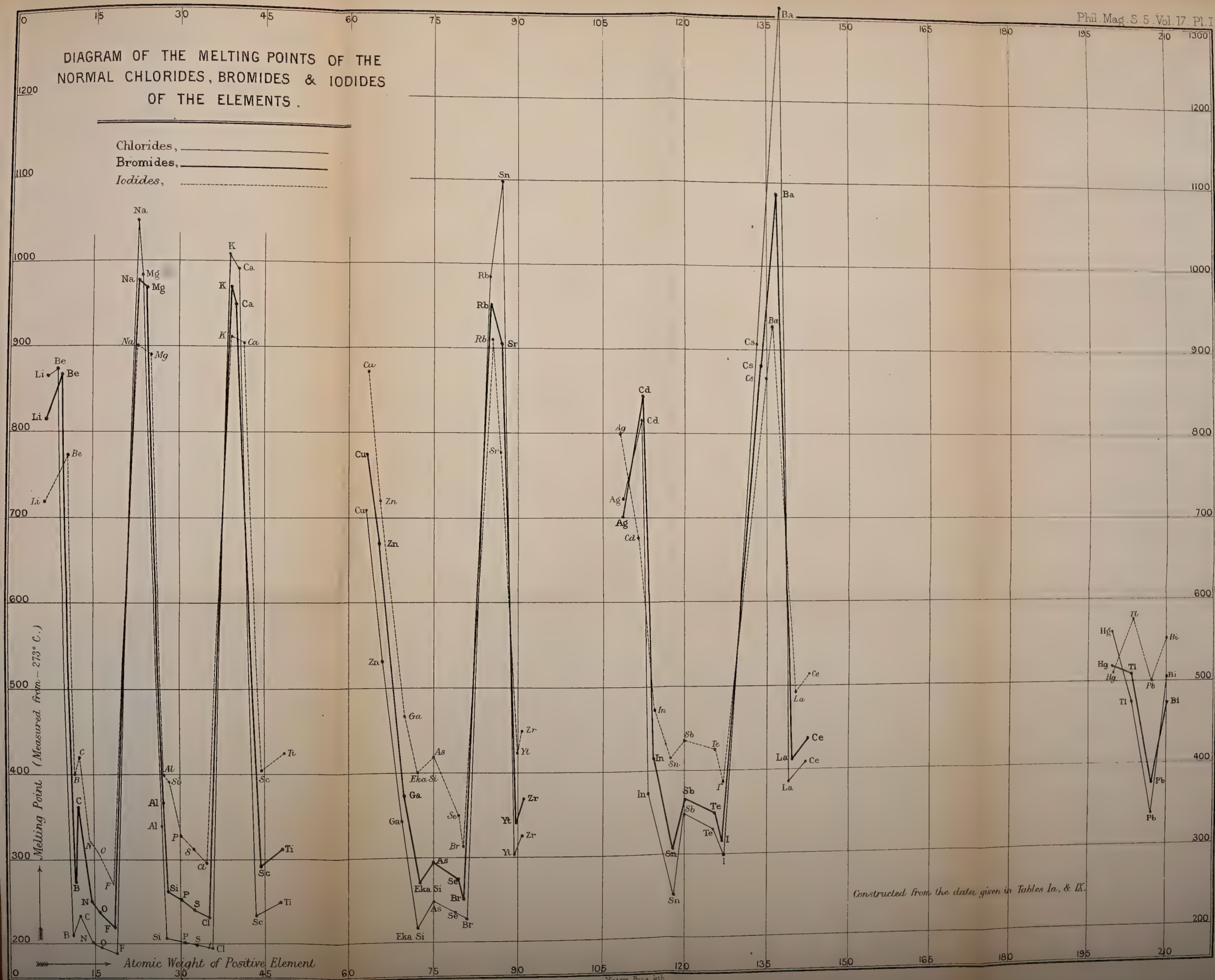
Constructed from the data given in Tables Ia., & IX.
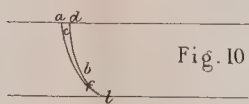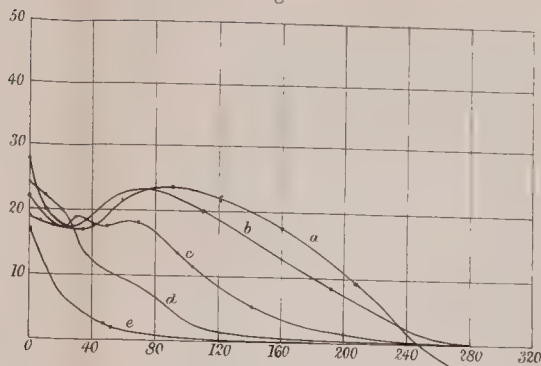
Mintern. Bros. lith.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4 a.

Fig. 4 b.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.
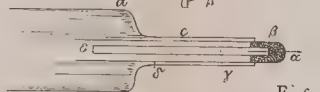
Fig. 14.
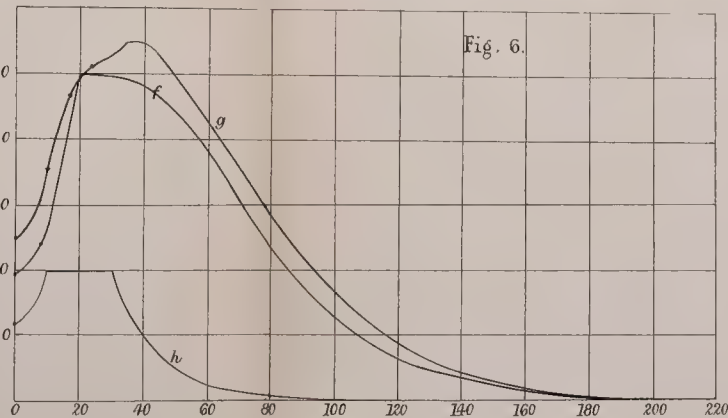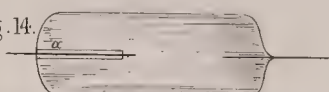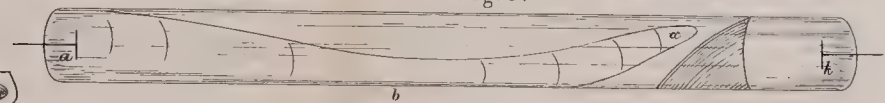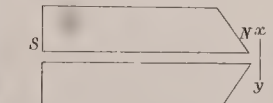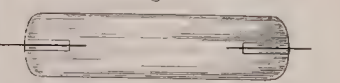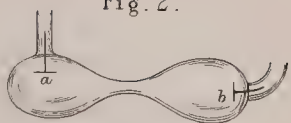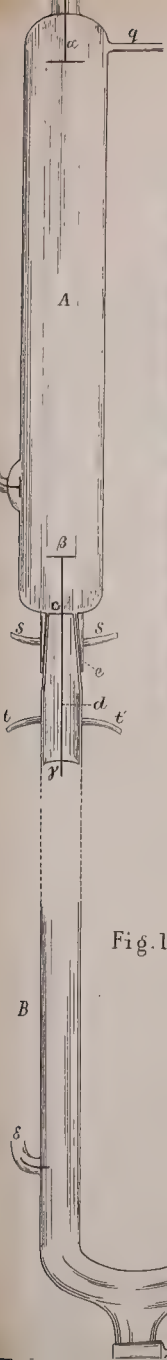
Fig. 1.
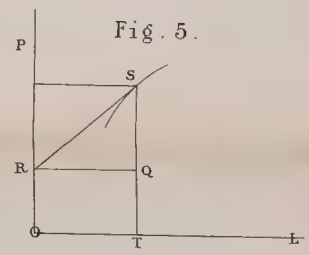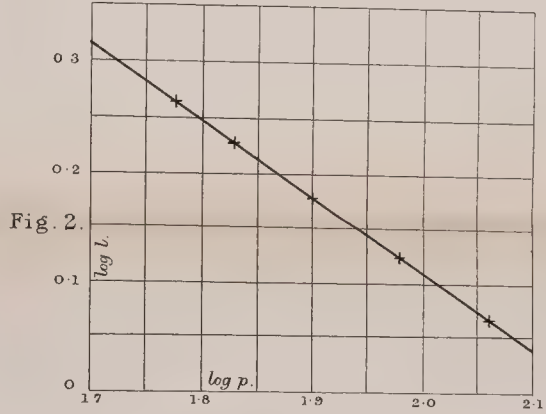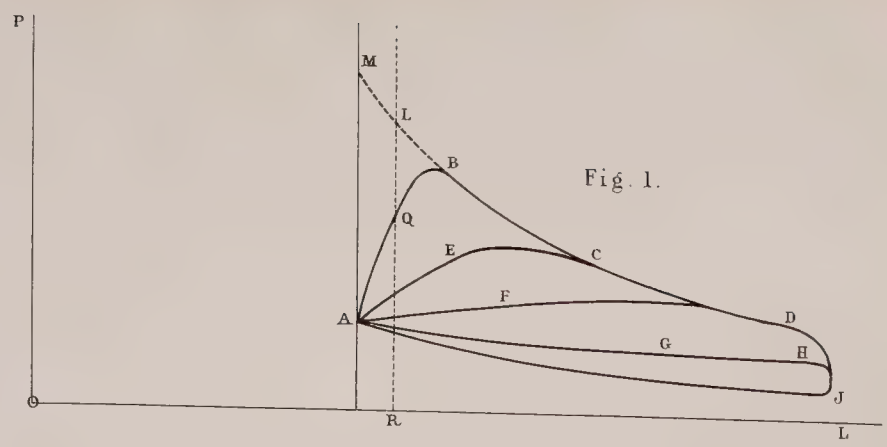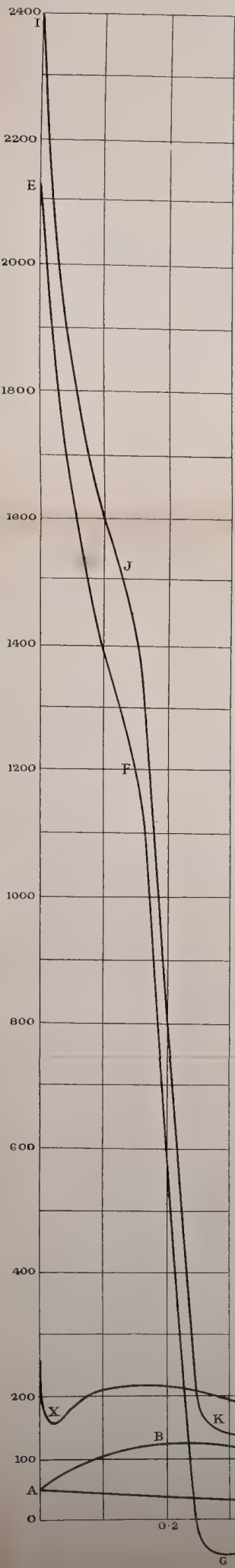
Fig. 2.
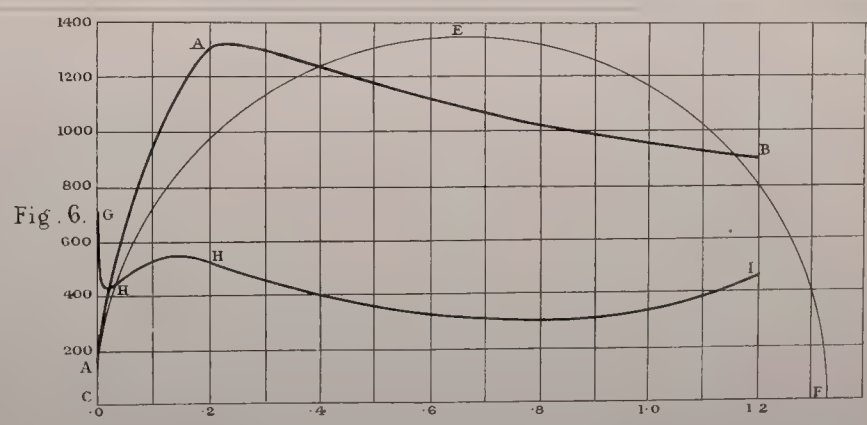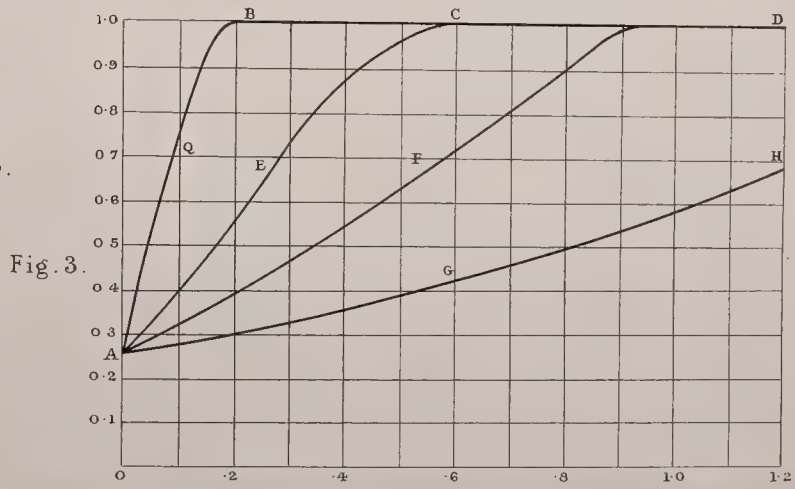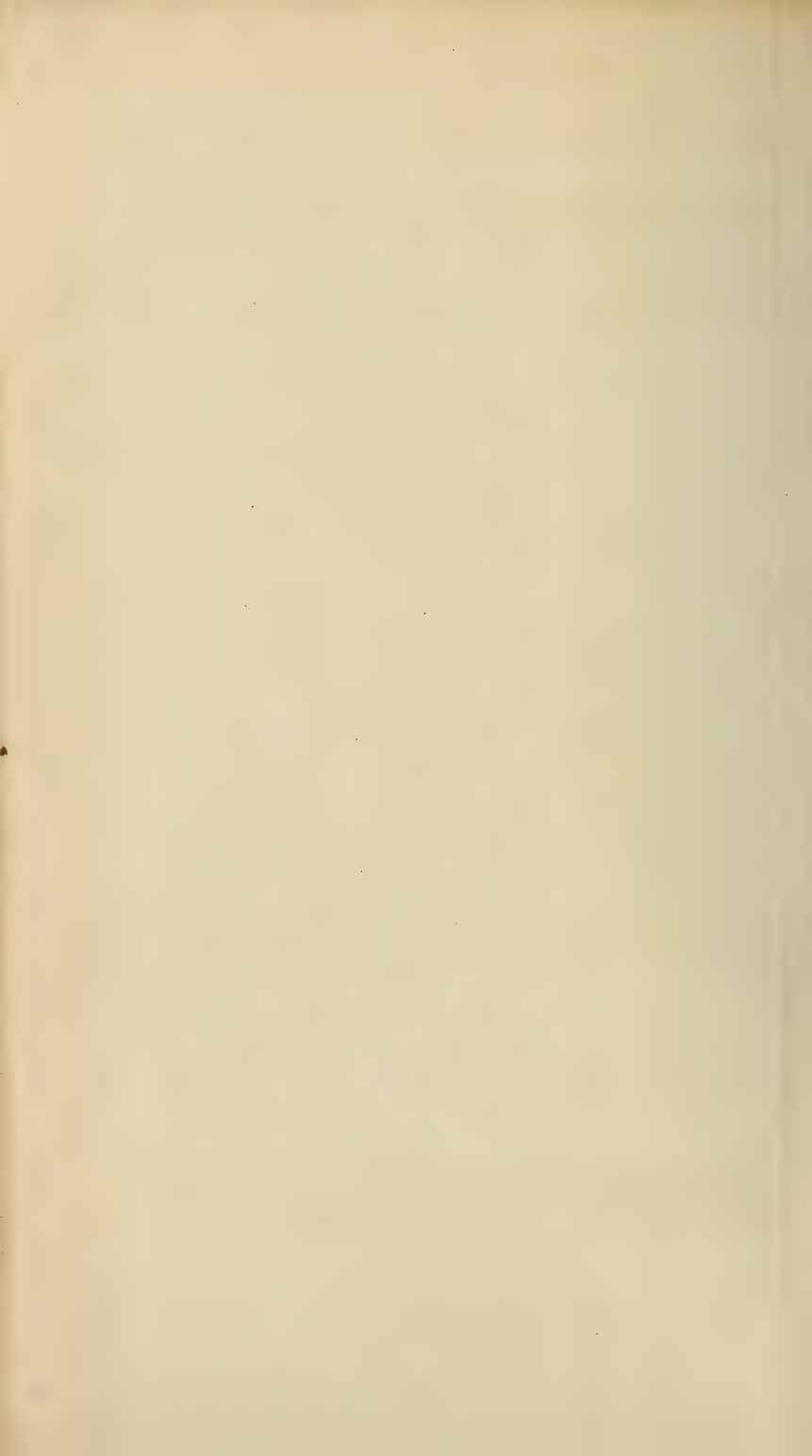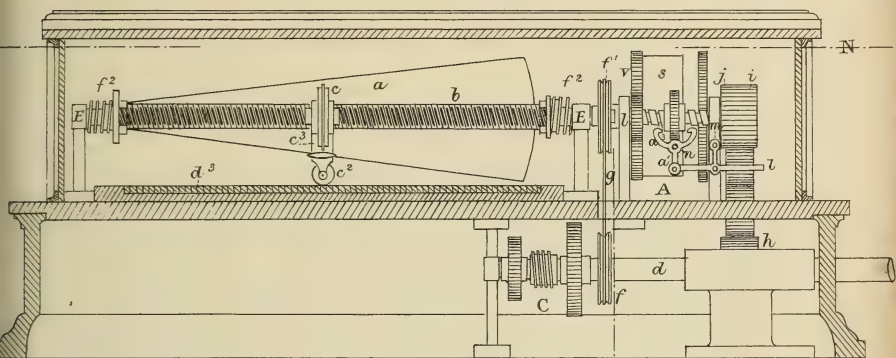
Fig. 5.

Fig. 4.

Fig. 3.

Fig. 6.

elevation.

clutch.

plan.

APPARATUS FOR COLOUR COMBINATIONS.

Plan of Box

Front Elevation of Box.

Side Elevation.

Scale ⅛.

Sliding frame carrying the incandescent wire. — Full size.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4

Fig. 5.

Cuprite.

Scale of Diameters.

VELOCITY of SOUND in AIR.

as deduced from experiments

made with

SMOOTH BRASS TUBES

Fig 1

Fig. 1.

Y

repulsion

attraction

P

O   M   N   X

Gas   Liquid

Solid

Fig. 8.

Fig. 2.

φ_n

φ_r

E_r

E_n

Fig. 5.

Y

repulsion

attraction

O   X

Fig. 3.

Y

repulsion

attraction

P

O   M   N   Q   X

Fig. 4.

Y

repulsion

attraction

O   N   G   X

Fig. 9.

A   B

C   D
O   F
E
M

P

Fig. 6.

A

B
C
D   E   F   G   H

K

Fig. 7.

B   C
P   A   Q

German-Silver (hard-drawn)

German-Silver (annealed)

(a)

(a)

Cu. No 4.

Al. No 1.

Cu No 4.

after 60 hours rest

Pb No 5.

after 18 hours rest

wire broke

wire broke

Mg No 1.

Zn { No 5

{ No 6

Fe No 3.

Magnesium No 1.

(2)

(1)

Zinc-Wires

wire broke

wire broke

No 5

No 6

.3123→
.3087→
.3188→
.3340→

(a)

(a)

(a)

(a)

Lead No 5.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

Fig. 14.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,
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